

Enhancement of Decolorization Rate and COD Removal from Dyes Containing Wastewater by the Addition of Hydrogen Peroxide under Solar Photocatalytic Oxidation

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Abstract

The solar photocatalytic decolorization and degradation of Maxoline Navy 2 RM 200% basic dye in aqueous solution with $\text{TiO}_2\text{-A}$ (pure anatase) as photocatalyst in a slurry form have been investigated using solar light. The removal of the dye was strongly enhanced by the addition of electron acceptors such as hydrogen peroxide (H_2O_2). The effects of various parameters such as amount of hydrogen peroxide, initial dye concentration, catalyst loading, pH-values on decolourization rate have been determined. The semi-logarithmic plots of absorbance data gave a straight line. The correlation constants for the fitted lines were calculated to be ranged from $r = 0.97$ to 0.99 . This finding indicates that the solar photocatalytic decolourization of the dye in aqueous TiO_2 suspensions can be described by the pseudo first-order kinetic model. The optimum operating conditions were to be: 1 g/L TiO_2 , 1.5 ml H_2O_2 , pH =3-5. The effect of dye-assisting chemicals such as Na_2CO_3 and NaCl has been also investigated. Addition of these chemicals inhibits the removal rate. At optimum operating conditions, color removal from the effluent reached 99.9% after 90 irradiation time. Measuring of Total Organic Carbon (TOC) loss showed that the dye was mineralized by 60% within this time and 75% within 240 irradiation time under these conditions indicating that the dye is also efficiently degraded. Nevertheless, the persistence of a low level of TOC indicated that mineralization was not complete and dead-end product(s) which was (were) resistant to solar photocatalytic oxidation might have accumulated.

Keywords: Solar photocatalytic degradation; solar energy; Basic dyes; Semi-conductor photo-catalyst (TiO_2), Electron acceptor (H_2O_2).

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1. Introduction

Textile industry needs large quantities of water of good quality in its fundamental processing steps, which generally imply the utilization of a large number of chemicals such as organic dyestuffs, surfactants, chelating agents, pH regulators, etc. These processes generate very toxic wastewater, whose treatment is often difficult due to the presence of some not biodegradable species with complex structure. Hence there is considerable current interest in developing alternative and more cost-effective methods.

In recent years advanced oxidation processes (AOPs) have been developed to meet the increasing need of an effective wastewater treatment. AOP generates powerful oxidizing agent hydroxyl radicals which completely destroy major classes of organic pollutants at ambient conditions. The combination of UV irradiation with photocatalysts is one of such methods which has attracted considerable attention in recent years, due to its effectiveness in mineralization (i.e. conversion to inorganic species) of organic compounds [1-2]. This has included removal of dye pollutants from residual textile treatment waters [3-5]. Heterogeneous photocatalysis through illumination of UV (or) solar light on a semiconductor surface such as TiO_2 is an attractive advanced oxidation process [6]. Such a UV- TiO_2 -based solar catalytic oxidation system exhibits some attractive characteristics. First, TiO_2 is stable, insoluble, non-toxic and environmentally acceptable by being fairly inert biologically and chemically. Second, TiO_2 is inexpensive reusable. Third, the photocatalyst titanium dioxide (TiO_2) is a wide band gap semiconductor (3.2 eV), has high photoactivity and is successfully used as a photocatalyst for the treatment of organic [7-8] and dye pollutants [9-12]. A further important advantage is the fact that the process can be powered by natural sunlight. Photodegradation of pollutants using TiO_2 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 [13-14]. Solar photocatalytic oxidation also appears to be a better treatment method for dyes-containing wastes than conventional biological processes [15-16]. While these compounds are highly recalcitrant to biodegradation [17], they can be destroyed by solar catalytic oxidation within hours [18]. Furthermore, during the anaerobic digestion stage of the conventional biological treatment process, the dyes can be readily transformed to other intermediates which are usually more toxic than the parental dyes. Solar catalytic oxidation, on the contrary, can oxidize these dyes efficiently to CO_2 and mineral ions [19].

Taking the above-mentioned concept into account, the present study was focused on oxidation of Maxilon Navy 2 RM 200% as basic dye by solar photocatalysis. This dyestuff was provided from Ciba, Switzerland and used throughout the present investigation as received and without further purification. The selection of textile wastewater was due to its recalcitrant and even toxic nature in conventional biotreatment. The dye is highly water-soluble and can be used for dyeing and printing acrylic fibers. For the practical application of dye wastewater by TiO_2 -sunlight process, there is a need to determine the optimal conditions of experimental parameters. The effects of various physico-chemical conditions on the degradation of the dye by solar photocatalytic oxidation were studied to find out the optimum conditions for removal of color and aromatic part of the dye.

2. Experimental

All solar photocatalytic experiments were carried out under similar conditions on sunny days of summer (August-September) under clear sky between 11 a.m. and 3 p.m. The intensity of solar radiation was measured using Weather Station erected in the test field of Solar Energy Department of NRC, Egypt. The problem of variation of intensity of sunlight even under clear sky is overcome by conducting experiments in sets simultaneously and comparing the results. At this time, the UV intensity ranged from 3.5

to 4 W/m^2 , which corresponds to the 30% of the power of the solar irradiation. The parabola cylindrical concentrator configuration, as reported in Figure (1), used to perform heterogeneous photocatalysis oxidation of the dye under solar irradiation in a total recirculation loop with a feed tank. The solar reactor consisted of one UV transparent glass tube ($3.5 \text{ m} \times 40 \text{ mm ID}$) with an irradiated surface of 3.7 m^2 placed on fixed support inclined 30° (latitude) with respect to the horizontal plane and facing south, in order to maximize the daily absorption of solar radiation [20]. The photocatalytic oxidation (PCO) was carried out in aqueous suspensions of TiO_2 irradiated by sunlight which was focused on the photoreaction system. The solution of dye and the catalyst at definite concentrations was continuously fed to the solar reactor from the feed tank by means of a peristaltic pump. The solution flow rate, maintained constant for all of the runs, was 60 L/h . The total volume, V_1 , of suspension charged in the whole system was 4 L , whereas the irradiated volume, V_i , i.e. the volume of suspension contained in the glass tubes, was 3.5 L . For all the solar photoreactivity experiments titanium oxide ($\text{TiO}_2\text{-A}$) (pure anatase, particle size of $0.02 \mu\text{m}$, with a BET surface area of $10 \text{ m}^2/\text{g}$) was reagent powder and used as sources of photo-catalysts supplied from Merck. For the majority of runs the catalyst amount was of 1 g/L ; a few experiments were carried out by using amount of catalyst (varying from 0.25 g/L to 1.25 g/L). Since the literature reports that the presence of strong oxidant species can greatly enhance the photooxidation rate of organic compounds [18,21,22]. The influence of the presence of hydrogen peroxide, (H_2O_2 solution, 35% w/w in stable form provided by Merck) on the dye decolorization rate was also investigated. The dependence of dye solar photooxidation rate on the initial dye concentration; catalyst amount and initial pH was investigated.

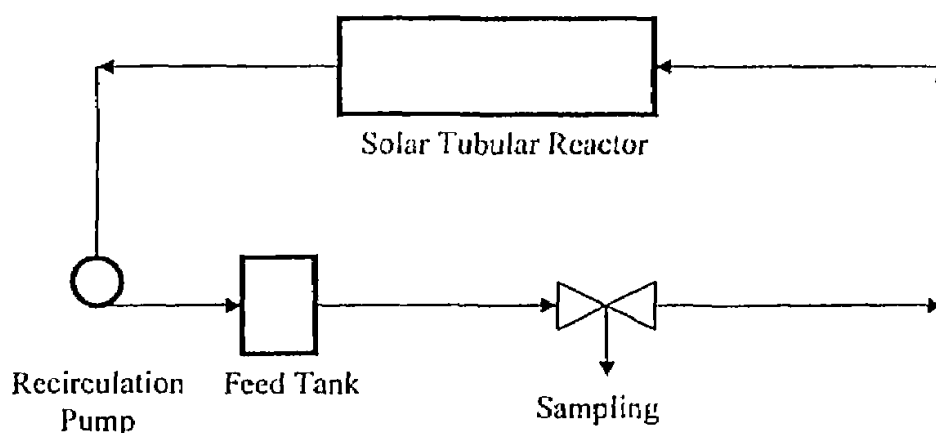


Figure (1) Schematic Diagram of Solar Catalytic Oxidation Unit

The experimental runs were carried out by using the following procedure: firstly the suspensions were magnetically stirred in the dark for 10 min to attain adsorption-desorption equilibrium between dye and TiO_2 , the aqueous suspension containing the dye and the TiO_2 powder was circulated in the reacting system, and then hydrogen peroxide was injected. Samples were taken at regular time intervals from the solar reactor and first were centrifuged to get rid off the residual catalyst and then were analyzed immediately

to avoid further reaction. For TOC determination, the reaction was stopped instantly by adding NaOH to the reaction samples to decompose any residual hydrogen peroxide and prevent hydrogen peroxide from reacting with dye during the analysis, since hydrogen peroxide cannot proceed at pH>10. The runs were carried out at different initial dye concentrations and most of them at the natural pH values of the suspensions at 7.1–7.4. Initial dye concentration of 100 ppm was chosen in most of experiments to simulate the high concentrations of such dyes in the industrial final effluent. Some additional runs were carried out by adjusting the initial pH to the desired value with H₂SO₄ or NaOH. The percent of color removal of the dye in the reaction mixture at different times was obtained by measuring absorbance at maximum wavelength ($\lambda_{max}=530$ nm) and computing the concentration from calibration curve. A PD-303 UV spectrophotometer (APEL Type), from Japan was employed for absorbance measurements. Hydrogen peroxide was detected by a modified iodometric titration method [23]. Total Organic Carbon (TOC) was measured using TOC Analyzer, Phonix 8000, from Japan.

3. Results and Discussion

By testing different kinetic models to the data of dye concentrations, it was found that solar photocatalytic oxidation of Maxilon Navy dye best fitted pseudo-first-order kinetics with respect to dye concentration, expressed by Equation (1):

$$-\frac{dC_{dye}}{dt} = k_{exp} * C_{dye} \quad \text{Equation (1)}$$

Where k_{exp} is the pseudo-first-order constant estimated from the experimental results. The integration of Equation (1) with the limiting conditions that at the start of the reaction ($t=0$) the dye concentration are equal to the initial one ($C_{dye} = C_{0,dye}$), gives:

$$C_{dye} = C_{0,dye} * e^{-(k_{exp} * t)} \quad \text{Equation (2)}$$

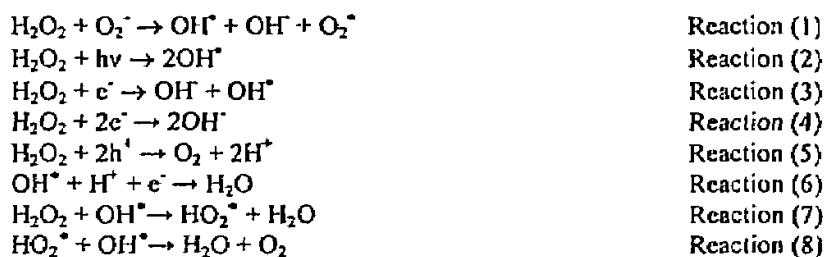
By applying a least-square best fitting procedure to the experimental data, the values of k_{exp} were determined. The photoreacting system used in this work is a total recycling one composed by a solar photocatalytic reactor and a feed tank. The reaction of dye oxidation occurs only inside the irradiated solar photocatalytic reactor. In order to obtain the true kinetic constants, the experimental reactivity data must be corrected by multiplying them by the ratio of the total volume (V_t) which represent the irradiated volume (V_i) + the dead volume of the connecting tubes and the holding tank, In the present case, being the kinetics of first order, the true kinetic constants (k_{true}) are obtained by the experimental ones (k_{exp}) by means of the simple relationships Equation (3) [22]. The calculated values of true kinetic constants for decolorization of the dye at different operating conditions are reported in Table (1).

$$k_{true} = k_{exp} * \frac{V_t}{V_i} \quad \text{Equation (3)}$$

The effect of addition of hydrogen peroxide, the initial dye concentration, amount of TiO₂, and pH on the solar photocatalytic decolorization rate was studied. Also the effect of presence of dye-assisting chemicals (Na₂CO₃; NaCl) as free hydroxyl radical's scavenger of has been investigated.

3.1. Effect of hydrogen peroxide addition

From separate experiments, it was observed that in non-irradiated suspensions the dark adsorption of dye on TiO₂ was slight (about 5% color removal). Figure (2) shows the kinetics of the disappearance of the dye under three conditions. There was a slightly observable increase in color removal of the dye (29%) when the solar irradiation was carried out in the absence of TiO₂. However, in the presence of TiO₂, an increase in color removal of dye (70%) occurred by solar irradiation. From the standpoint of solar collecting technology, this is a rather inefficient process, even considering for a high added value application [20]. The photocatalytic degradation of organic pollutants depends upon their reactions with the OH[•] radicals. Therefore, electron acceptors have been used to enhance the degradation rates since they generate OH[•] radicals [24]. Hydrogen peroxide (H₂O₂) is the most widely used electron acceptor. It is clear that, the solar photocatalytic oxidation process can be accelerated by H₂O₂ as demonstrated in some studies [13,25]. H₂O₂ serves two roles in solar photocatalytic oxidation to cause an enhancement effect. It can both act as a source of OH[•] by reacting with superoxide anion (O₂^{•-}) or by direct photolysis (Reactions (1) and (2)). Besides, it can act as a conduction-band electron acceptor forming OH[•] radicals subsequently (Reaction (3)). Being an electron acceptor, H₂O₂ does not only generate OH[•] radicals, but it also inhibits electron-hole recombination process (e⁻/h⁺), at the same time, which is one of the most important practical problems in using TiO₂ as a photocatalyst [2,6,27]. The enhancement of decolourisation and degradation by addition of H₂O₂ is due to an increase in the hydroxyl radical concentration as shown by Reactions (4-8).



As can be seen also from Figure (2), decolorization rate of Maxilon Navy 2RM dye was markedly enhanced by the addition of H₂O₂, as expected. Figure (3) exhibits the effect of initial amount of added hydrogen peroxide on the decolorization rate of the dye. As it can be seen from the straight lines obtained, the solar photocatalytic decolorization of the dye with the addition of H₂O₂ also follows the pseudo-first order kinetics. The apparent rate constant was also found to be dependent upon the concentration of H₂O₂. The values of the overall reaction rate constants with the correlation coefficients for each of the fitted lines tabulated in Table (1).

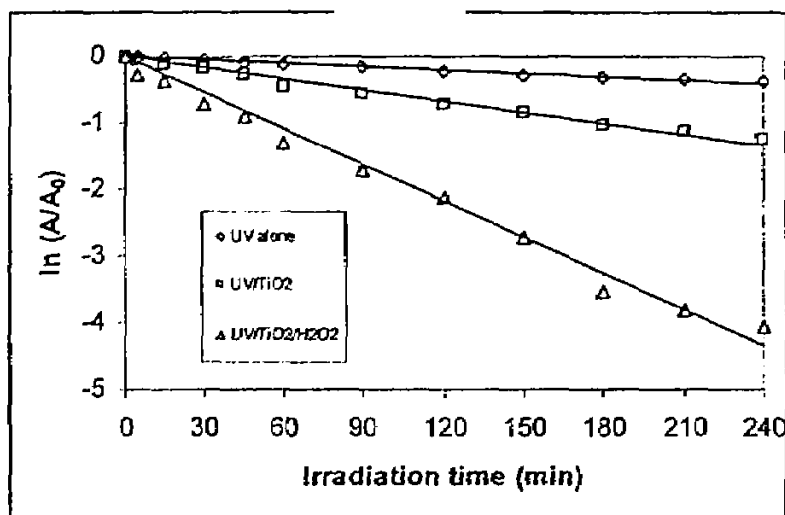


Figure (2) Effect of hydrogen peroxide addition on solar photocatalytic oxidation rate of Maxilon dye under solar irradiation. [Dye concentration=100ppm, TiO_2 concentration=1g/L, H_2O_2 = 1ml/L, pH=7.5].

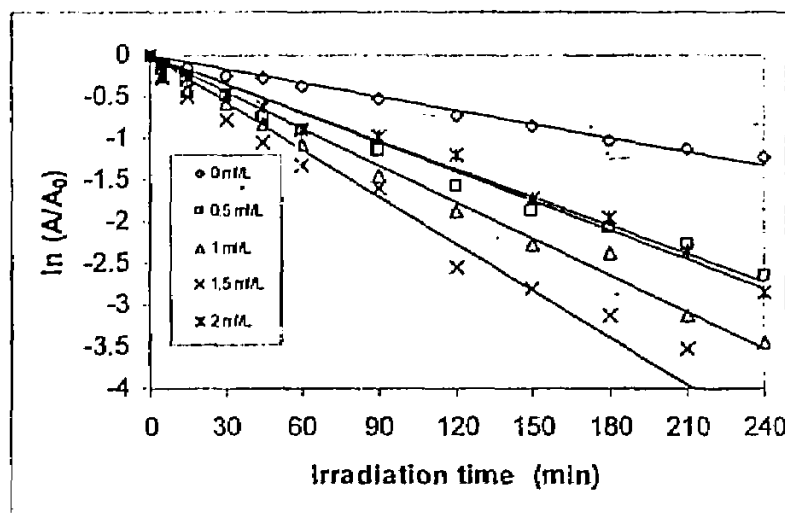


Figure (3) Effect of hydrogen peroxide concentration on decolorization of Maxilon dye under solar irradiation [Dye concentration=100 ppm, TiO_2 concentration=1g/L, pH=7.5].

As can be seen from Figure (3), the decolorization rate increases as the concentration of H_2O_2 increases. The pseudo-first-order rate constant increased by about 2-fold when H_2O_2 concentration changed from 0 to 0.5 ml/L. A little enhancement, however, was observed when the concentration further increased to 1 and 1.5 ml/L. A concentration of 1.5 ml/L appears to be optimal. Similar observations were also reported in previous studies where an increase in H_2O_2 level enhanced photo-catalytic oxidation rate up to an optimal point beyond which inhibition occurred [13,26]. As described before, However, when present at high concentration, H_2O_2 can also become a scavenger of valence-band holes (Reactions (4-5)) and OH^\bullet (Reactions (6-8)) [1,13]. Furthermore, H_2O_2 can be adsorbed onto TiO_2 particles to modify their surfaces and subsequently decrease its

catalytic activity [13]. Since the influence of H_2O_2 , has been in some cases controversial and it appeared strongly dependent on substrate type and on various experimental parameters its usefulness must be accurately checked under the described operative conditions.

3.2. Effect of initial dye concentration

At a fixed weight of TiO_2 and pH, the effect of initial dye concentrations ranging from 40 to 100 mg/L on decolorization of Maxilon Navy dye by photocatalytic was investigated under solar irradiation. A plot of $\ln(A/A_0)$ versus solar irradiation time from such experiments yields straight lines (Figure 4); from the slopes, the rate constants k_{exp} (min^{-1}) can be evaluated. The initial dye concentrations versus rate data are given in Table (1).

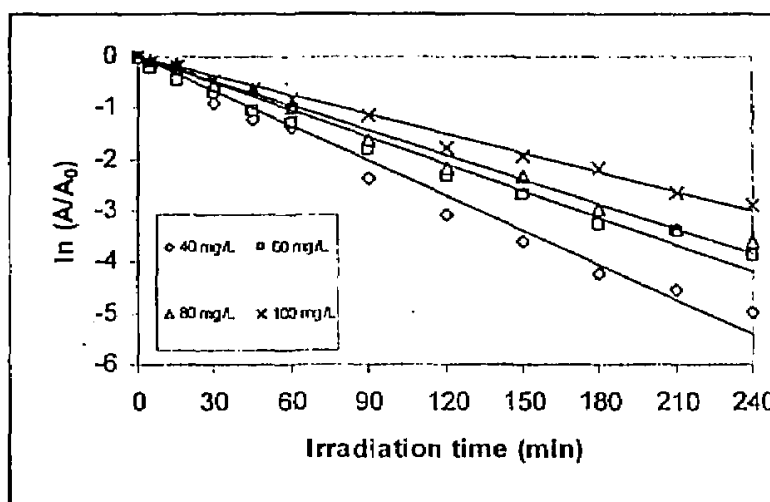


Figure (4) Effect of initial dye concentrations on decolorization of Maxilon dye under solar irradiation [TiO_2 concentration=1g/L, H_2O_2 =1ml/L, pH=7.5].

As depicted in the Figure, a decrease in the rate constant was observed upon the increase of initial dye concentration. Similar observations have also been reported for the PCO of other dyes and organic compounds [28,29,25]. One possible cause for such results is the solar radiation-screening effect of the dye itself. At a high dye concentration, a significant amount of solar radiation may be absorbed by the dye molecules rather than the TiO_2 particles, consequently, by increasing the initial dye concentration, the photon flow reaching the catalyst particles decreased due to the fact that increasing numbers of photons were absorbed by the dye molecules present in the solution and/or on the catalyst surface, and thus reduces the efficiency of the catalytic reaction [18]. Another possible cause is the interference from intermediates formed upon solar photocatalytic of the parental dye. These intermediates may include aromatics, aldehydes, ketones and organic acids as shown by previous studies with various aromatic compounds [30-32]. They may compete with the dye molecules for the limited adsorption and catalytic sites on the TiO_2 particles [33] and thus inhibit decolorization. Such suppression would be even more pronounced in the presence of an elevated level of

degradation intermediates formed upon an increased initial dye concentration. Although we have not identified in our study, the intermediates formed during the solar photocatalytic oxidation of Maxilon Navy dye, their occurrence was clearly indicated by the presence of about 75% of total organic carbon (TOC) remaining when more than 99.5% of the dye was decolorized.

3.3. Effect of catalyst loading

The effect of TiO_2 loading on decolorization rate is presented in Figure (5). In the absence of the catalyst, about 50% color removal was observed after 4 hours irradiation time. Decolorization started to increase when 0.2 g/L of TiO_2 was added and the rate increased sharply with catalyst loading up to 0.8 g/L. However, only a slight enhancement was observed when TiO_2 concentration further increased to 1 g/L. Similar observations were also reported in other studies on dyes and various organics [28,29,34]. As the concentration range increases from 0.2 to 1 g/L, the number of photons absorbed and the number of dye molecules adsorbed are increased owing to an increase in the number of catalyst particles. The density of particles in the area of illumination also increases and so the rate is enhanced. The observed enhancement in decolorization is probably due to an increased number of available adsorption and catalytic sites on TiO_2 . At a certain level, the number of available substrate molecules is insufficient for adsorption by the increased number of TiO_2 particles, i.e. although more area is available, for constant initial dye concentration, the number of substrate molecules present in the solution remains the same. Hence, above a certain level, additional catalyst powder is not involved in catalyst activity and the rate tends to level off. Maximum decolorization was obtained at a TiO_2 concentration of 1 g/L.

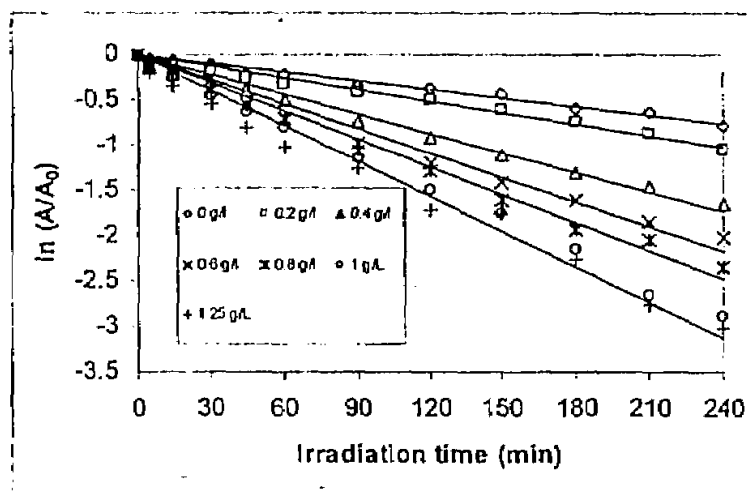


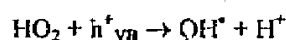
Figure (5)-Dependence of the photocatalytic decolorization rate of Maxilon dye on the amount of TiO_2 under solar irradiation [Dye concentration=100 ppm, $\text{H}_2\text{O}_2=1\text{ml/L}$, $\text{pH}=7.5$].

A further increase beyond this optimum catalyst loading as shown in Figure (5), however, may cause light scattering and screening effect and thus reducing the specific activity of the catalyst [29]. In addition, at high TiO_2 concentrations, particles aggregate

which reduces the interfacial area between the reaction solution and the photocatalyst. Thus, the number of active sites on the catalyst surface is decreased. Agglomeration and sedimentation of the TiO₂ particles were observed in our study when more than 1g/L of TiO₂ was added to the dye solution. In such a condition, part of the catalyst surface probably became unavailable for photon absorption and dye adsorption, thus bringing little stimulation to the catalytic reaction and may be the other reasons for the decrease in the decolorization rate.

3.4. Effect of initial pH values

The most important parameter that influences the photocatalytic degradation is solution pH. Previous studies indicate that pH may affect photocatalytic oxidation in a number of ways. First, the charge of the dye molecules and the surface of the TiO₂ catalyst are both pH dependent. pH changes can thus influence the adsorption of dye molecules onto the catalyst surfaces, an important step for photocatalytic oxidation to take place [35]. Second, as indicated in Reaction (9), OH[•] can be formed by the reaction between hydroxide ion and positive hole. An alkaline condition would thus favor OH[•] formation and enhance degradation. Third, the TiO₂ particles tend to agglomerate under acidic condition and the surface area available for dye adsorption and photon absorption would be reduced [35].



Reaction (9)

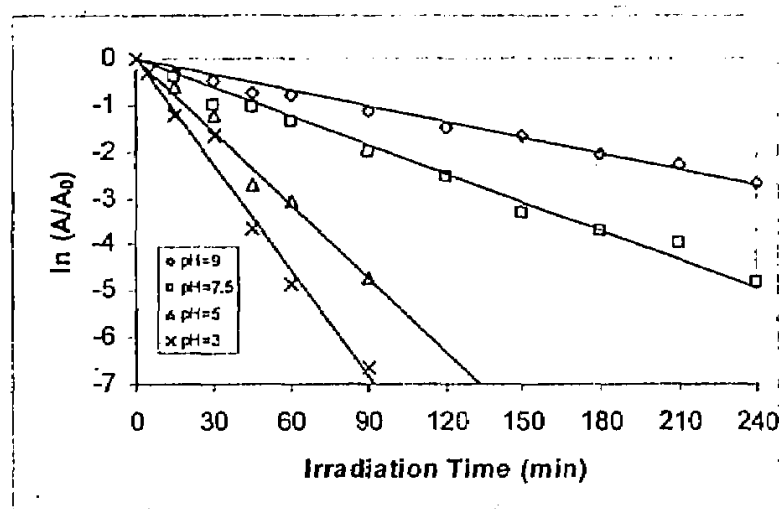


Figure (6) Effect of pH values on decolorization of Maxilon dye under solar irradiation [Dye concentration=100 ppm, TiO₂ concentration=1g/L, H₂O₂=1ml/L].

The effect of pH in the presence hydrogen peroxide was also investigated, at the conditions which were shown to bring the greatest enhancement to decolorization. Figure (6) shows the effect of pH on the decolorization of Maxilon Navy dye in the presence of 1g/L of TiO₂ and 1.5 ml/L hydrogen peroxide. The results, however, were very different

from those obtained with other works by using titanium dioxide only without addition of H_2O_2 [36,25] at acidic conditions. As seen in Figure (6), the highest decolorization rate was observed at pH 3–5 and the pseudo-first-order rate constant decreased with the increase of pH values. This can be attributed to that the acidic medium is favorable to hydrogen peroxide, since hydrogen peroxide cannot precede at high pH values. At this point, we cannot explain why only the significant interaction between pH and concentration of TiO_2 or H_2O_2 in the solar photocatalytic degradation of the dye; and how the elevated TiO_2 and H_2O_2 concentrations would have such a different impact on the optimal pH of the solar photocatalytic reaction. A more thorough study will be undertaken to seek an explanation for such observations.

3.5. Effect of the presence of NaCl and Na_2SO_4

Some anions commonly found in natural or polluted waters (e.g., chloride, bromide, sulphate, phosphate) have an inhibiting effect on the photodegradation process if they are bound to TiO_2 or close to its surface [37]. The other chemicals used in the dye industry play a vital role in the dyeing process. Some experiments were also performed in the presence of NaCl or Na_2SO_4 ions. Indeed these ions are usually present in real wastewater produced by textile industry, as they are added to the liquor used for performing the operation of scouring (i.e. the treatment that removes wax, dirt, grease and other natural impurities from the fibers before the dyeing process). Na_2CO_3 is added to adjust the pH of the dye bath which is important in fixing the dye on the fabrics and in the fastness of colour. Sodium chloride is mainly used in the dyeing process for the transfer of dye stuff to fabric [38]. Therefore, the dye industry wastewater contains a considerable amount of carbonate and chloride ions. Hence, it is important to study the influence of CO_3^{2-} and Cl^- ions in the solar photocatalytic degradation. The experimental results indicated that the reactivity results indicated that these species significantly affect the solar photoreactivity of the dye. At the examined concentration (5 g/L), the experimental results indicated that these chemicals inhibit the removal rate to the half of that in optimum operating conditions. Similar observations have been reported earlier in the literature [39]. The decrease in decolorization efficiency of the dye is due to hydroxyl radical scavenging property of carbonate ion and also the hole scavenging properties of chloride ion as shown in the following Reactions:



3.6. Degradation of Maxilon Navy dye under optimal conditions

Based on the results obtained in the characterization experiments, the optimal conditions for the photocatalytic oxidation of Maxilon Navy dye under solar radiation were found to be: TiO_2 concentration, 1 g/L; H_2O_2 concentration, 1.5 ml/L; pH, 5.0. Degradation and mineralization of Maxilon Navy by solar photocatalytic oxidation under such conditions was studied by measuring Total Organic Carbon (TOC) of the dye solution. Figure (7) shows the changes of color and TOC removal in the reaction solution

during the solar photocatalytic oxidation process of the dye at optimum operating conditions. As indicated, the dye was decolorized by about 99% within the first 90 min. and remained almost unchanged within the same period of time till 99.9 within 240 min. TOC removal reached 60% within 90 min irradiation time, indicating the formation of organic intermediates derived from the dye. The % TOC removal then increased with time but very slowly till a constant level (75%) up to 240 min of solar irradiation. These results indicate that the fast decolorized dye was followed by much slower mineralization of intermediates formed subsequently. On the other hand, the persistence of a low but constant TOC removal in solution suggests the accumulation of dead-end product (s) which is (are) resistant to degradation by the solar photocatalytic oxidation reaction. Therefore, it should be readily removed by biological treatment systems and is unlikely to pose a problem to the environment.

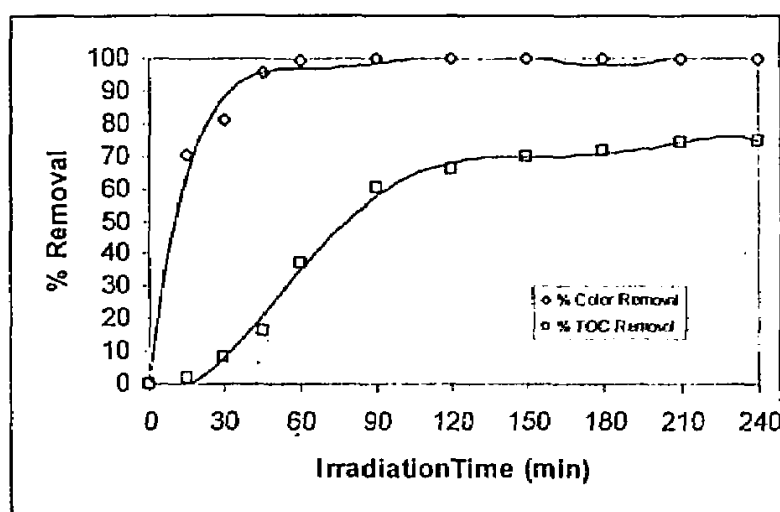


Figure (7) Color and TOC removal during the solar photocatalytic oxidation of Maxilon Navy dye under optimal conditions. [Dye concentration=100 ppm, TiO_2 =1g/L, H_2O_2 =1ml/L, pH=5].

4. Conclusions

This study investigated the solar photocatalytic oxidation of Maxilon Navy 2 RM 200% basic dye by using titanium dioxide. The decolorization reaction kinetics followed the pseudo-first-order rate. The decolorization rate of Maxilon Navy 2RM dye was markedly enhanced by the addition of H_2O_2 . Optimal physico-chemical conditions for the degradation a 100-mg/L dye solution, under solar photocatalytic oxidation, were determined to be: TiO_2 concentration, 1 g/L; initial H_2O_2 concentration, 1.5 ml/L; initial pH, 5. Under these conditions, the dye can be decolorized by 99.9% mineralized with a TOC removal of 75% within 240- min. The presence of auxiliary chemicals such as Na_2CO_3 and $-NaCl$ decreases the photocatalytic decolorization. The efficient decolorization and mineralization respectively indicate that solar photocatalytic oxidation can be used as a simple, efficient and economic treatment of wastewater containing basic dye. Mineralization, however, was not complete probably due to presence of intermediates compounds resistance to degradation by the TiO_2 -mediated solar catalytic oxidation reaction.

Table (1). Values of % color removal, reaction rate constant and correlation factor at experimental operating conditions for the solar photocatalytic oxidation for Maxilon Navy dye.

[Dye] ₀ mg/L	[H ₂ O ₂] ₀ m/L	[TiO ₂] ₀ g/L	pH ₀	% Color Removal	k _{exp} (min ⁻¹)	Correlation Factor (r)
100	0	0	7.5	26.8	0.001	0.98
100	0	1	7.5	70.4	0.006	0.981
100	0.5	1	7.5	92.9	0.012	0.976
100	1	1	7.5	96.8	0.015	0.985
100	1.5	1	7.5	99.3	0.019	0.974
100	2	1	7.5	94.1	0.011	0.991
100	1.5	0	7.5	53.9	0.003	0.975
100	1.5	0.2	7.5	59.6	0.004	0.977
100	1.5	0.4	7.5	80.9	0.007	0.98
100	1.5	0.6	7.5	86.7	0.009	0.975
100	1.5	0.8	7.5	90.5	0.01	0.986
100	1.5	1	7.5	94.4	0.012	0.994
100	1.5	1.25	7.5	95	0.013	0.978
40	1.5	1	7.5	99.1	0.023	0.982
60	1.5	1	7.5	97.9	0.017	0.973
80	1.5	1	7.5	97.2	0.016	0.99
100	1.5	1	9	92	0.011	0.98
100	1.5	1	5	99.9	0.052	0.984
100	1.5	1	3	99.9	0.075	0.985

Where, [Dye]₀ is the initial dye concentration, [H₂O₂]₀ is the initial H₂O₂ concentration, [TiO₂]₀ is the amount of TiO₂, pH₀ is the adjusted initial value of pH, % Color Removal after 240 minutes irradiation time and k_{exp} is the experimental value of the pseudo-first-order reaction rate constant.

References

- [1] Legrini O, Oliveros E, Braun AM., "Photochemical processes for water treatment". Chem Rev 93 (1993) 671-98.
- [2] Turchi C.S., Ollis D.F., Turchi C.S., "Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack". J. Catal. 122 (1990) 178-192.
- [3] Hachem C., Bocquillon F., Zahraa O., Bouchy M., "Decolourization of textile industry wastewater by the photocatalytic degradation process". Dyes Pigments 49 (2001) 117-25.
- [4] Arslan I., Balcioglu IS., Bahnemann DW., "Advanced chemical oxidation of reactive dyes in simulated dyehouse e.uents by ferrioxalate-Fenton/UV-A and TiO₂/UV-A processes". Dyes Pigments 47 (2000) 207-18.
- [5] Rodriguez M., Sarria V., Esplugas S., Pulgarin C., "Photo-Fenton treatment of a biorecalcitrant wastewater generated in textile activities: biodegradability of the phototreated solution". J. Photochem. Photobiol. A 151 (2002) 129-135.
- [6] Hofmann MR., Martin ST., Choi W., Bahnemann DW., "Environmental applications of semiconductor photocatalysis". Chem. Rev. 95 (1995) 69-96.
- [7] Vorontsov VA., Dubovitskaya-VP., "Selectivity of photocatalytic-oxidation of gaseous ethanol over pure and modified TiO₂". J Catal., 221 (2004) 102-9.
- [8] Heredia J.B., Torregrosa J., J.P., Dominguez J.A. Peres, Oxidation of p-hydroxybenzoic acid by UV radiation and by TiO₂/UV radiation: comparison and modelling of reaction kinetic, J. Hazard. Mater. B 83 (2001) 255-264.

- [9] Chen D., Ray A.K., "Photodegradation kinetics of 4-nitrophenol in TiO₂ suspension". *Water Res.* 32 (1998) 3223–3234.
- [10] Saquib M, Muncer M. Titanium dioxide mediated photocatalysed degradation of a textile dye derivative, acid orange 8, in aqueous suspensions. *Desalination* 2003;155:255-63.
- [11] Epling G.A., Lin C., "Photoassisted bleaching of dyes utilizing TiO₂ and visible light". *Chemosphere* 46 (2002) 561–570.
- [12] Bauer C., Jacque, P., Kalt, A., "Photooxidation of an azo dye induced by visible light incident on the surface of TiO₂". *J. Photochem. Photobiol. A: Chem.* 140 (2001) 87–92.
- [13] Malato S., Blanco J., Richter C., Braun B., Maldonado, M.I., "Enhancement of the rate of solar photocatalytic mineralization of organic pollutants by inorganic oxidizing species". *Appl. Catal. B: Environ.* 17: 4 (1998) 347–356.
- [14] Bandala E.R., Gelover S., Leal M.T., Arancibia-Bulnes C., Jimenez A., Estrada C.A., "Solar photocatalytic degradation of Aldrin". *Catal. Today* 76 (2002) 189–199.
- [15] Wang, Y., "Solar photocatalytic degradation of eight commercial dyes in TiO₂ suspension". *Water Res.* 34: 3 (2000) 990–994.
- [16] Neppolian, B., Choi H.C., Sakthivel, S., Arabindoo, B., Murugesan, V., "Solar/UV-induced photocatalytic degradation of three commercial textile dyes". *J. Hazardous Mater. B* 89 (2002b) 303–317.
- [17] Dai S., Zhuang Y., Chen Y. and Chen L. "Study on the relationship between structure of synthetic organic chemicals and their biodegradability". *Environmental Chemistry* 14 (1995) 354–367.
- [18] Mills, A., Davis, R.H., and Worsley, D. "Water purification by semiconductor photocatalysis". *Chemical Society Reviews* 22 (1993), pp. 417–434.
- [19] Tang W.Z., Zhang Z., An H., Quintana M.O. and Torres, D.F., "TiO₂/UV photodegradation of azo dyes in aqueous solutions". *Environmental Technology* 18 (1997) 1–12.
- [20] Amany M. Fathy, Joseph Y. Farah and Montaser Y. Ghaly, "Effect of Catalyst Type and Dose on Solar Photocatalytic Oxidation for the Degradation of Zenafix Yellow Reactive Dye Aqueous Solution", *AFINIDAD*, Vol. 63, N. 521, January-February (2006) (In press).
- [21] Tanaka K., Hisanaga T., Harada K., "Photocatalytic Degradation of Organohalide Compounds in Semiconductor Suspension with Added Hydrogen Peroxide". *New J. Chem.* 13 :1 (1989) 5–7.
- [22] Augugliaro V., Davi E., Palmisano L., Schiavello M., Sclafani A., "Influence of Hydrogen Peroxide on the Kinetics of Phenol Photodegradation in Aqueous Titanium Dioxide Dispersion". *Appl. Catal.* 65 (1990) 101–116.
- [23] Vogel A.I., *A Text-Book of Quantitative Inorganic Analysis*, Third Edition, (1961) 05-206, LONGMAN.
- [24] Al-Ekabi H., Butters B., Delary D., Ireland J., Lewis N., Powell T., Story J., Ollis D.F. "Photocatalytic Purification and Treatment of Water and Air". Elsevier, Amsterdam, 1993, pp. 321–335.

- [25] Poullos and Aetopoulou, 1999 Poullos I. and Aetopoulou I., "Photocatalytic degradation of the textile dye Reactive Orange 16 in the presence of TiO₂ suspensions". *Environmental Technology* 20 (1999) 479–487.
- [26] Grätzel C.K., Jirousek M., Grätzel M., "Decomposition of Organophosphorous Compounds on Photoactivated TiO₂ Surfaces". *J. Mol. Catal.* 60 (1990) 375–387.
- [27] Poullos I. and Tsachpinis I., "Photodegradation of the textile dye Reactive Black in the presence of semiconducting oxides". *Journal of Chemical Technology and Biotechnology* 74 (1999) 349–357.
- [28] Davis R.J., Gainer J.L., O'Neal G. and Wu I., "Photocatalytic decolorization of wastewater dyes". *Water Environment Research* 66 (1994) 50–53.
- [29] Lea J. and Adesina A.A., "The photo-oxidative degradation of sodium dodecyl sulfate in aerated aqueous TiO₂ suspension". *Journal of Photochemistry and Photobiology A: Chemistry* 118 (1998) 111–122.
- [30] Serpone N., Terzian R., Mincro C. and Pelizzetti E., "Heterogeneous photocatalyzed oxidation of phenol, cresols, and fluorophenols in aqueous suspensions". In: C. Kotal and N. Serpone, Editors, *Photosensitive Metal-Organic Systems: Mechanistic Principles and Applications*, American Chemical Society, New York, USA (1993) 281–314.
- [31] d'Hennezel O., Pichat P. and Ollis D.F., "Benzene and toluene gas-phase photocatalytic degradation over H₂O and HCl pretreated TiO₂: by-products and mechanisms". *Journal of Photochemistry and Photobiology A: Chemistry* 118 (1998) 197–204.
- [32] Tanaka K., Padermpole K. and Hisanaga T., "Photocatalytic degradation of commercial azo dyes". *Water Research* 34 (2000) 327–333.
- [33] Ollis D.F., Pelizzetti E. and Serpone N., "Heterogeneous photocatalysis in the environment: application to water purification". In: N. Serpone and E. Pelizzetti, Editors, *Photocatalysis: Fundamentals and Applications*, Wiley, New York, USA (1989) 603–637.
- [34] Goncalves M.S.T., Oliveira-Campos A.M.F., Pinto E.M.M.S, Plasência P.M.S. and Queiroz M.J.R.P., "Photochemical treatment of solutions of azo dyes containing TiO₂". *Chemosphere* 39 (1999) 781–786.
- [35] Fox M.A. and Dulay M.T., "Heterogeneous photocatalysis". *Chemical Reviews* 93 (1993), pp. 341–357.
- [36] Tang W.Z., and An H., "Photocatalytic degradation kinetics and mechanism of Acid Blue 40 by TiO₂/UV in aqueous solution". *Chemosphere* 31 (1995) 4171–4183.
- [37] Herrmann J.M., Guillard C. and Pichat P., "Heterogeneous photocatalysis: an emerging technology for water treatment". *Catalysis Today*, 17 (1993) 7-20.
- [38] Pelizzetti, E., "Concluding remarks on heterogeneous solar photocatalysis". *Solar energy materials and solar cells* 38 (1995) 453-457.
- [39] Wang, K.H., et al. "The pH and anion effects on the heterogeneous photocatalytic degradation of O-methylbenzoic acid in TiO₂ aqueous suspension". *Chemosphere*, 40 (2000) 389-394.