Photocatalytic Degradation of a Chemical Industry Wastewater: Search for Higher Efficiency

Reza Sarkhanpour1, Omid Tavakoli1*, Samira Ghiyasi2, Mohammad Reza Saeb3*, Rafael Borja4

1School of Chemical Engineering, College of Engineering, University of Tehran, Tehran 14176, Iran
2Department of Environmental Engineering, Central Tehran Branch, Islamic Azad University, Tehran, Iran
3Department of Resin and Additives, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran
4Instituto de la Grasa (CSIC), Campus Universidad Pablo de Olavide, building 46, Ctra. de Utrera km 1, 41013-Sevilla, Spain
*otavakoli@ut.ac.ir; *saeb-mr@icrc.ac.ir & mrsaeb2008@gmail.com

Abstract
In the present research, an annular photocatalytic reactor system was designed and operated to quantify the degradation of a real case chemical company wastewater. The photocatalytic degradation process was analyzed and optimized varying some critical operating variables such as pH, catalyst (TiO2) loading, H2O2 concentration (oxidant agent) and light intensity to find the best criterion warranting a high level of degradation. It was demonstrated that a pH of 7.0 and an amount of 2.0 g/L of TiO2 resulted in a cleanup allowable level for discharge to river. Furthermore, photo-degradation by H2O2/TiO2/UV process was much more efficient (97%) with respect to the processes carried out individually by H2O2/UV(92%) or TiO2/UV (89%). It is remarkable that the optimum concentration of H2O2 was 11.6 mM, and increasing the intensity of light accelerated degradation reaction. Careful selection of industrial wastewater reflected the capability predicting the level of contamination of wastewaters.

Keywords
Wastewater Treatment; Photocatalytic Degradation; Chemical Company Wastewater; TiO2 Catalyst; Photodegradation

1. Introduction
The progress in the chemical industry has always been associated with significant negative impacts to the environment. Fortunately, sufficient effort has been meanwhile spent by the researchers and engineers alike to design and development of novel strategies relating to environmental cleanup. From the perspective of toxicity, wastewaters of industrial plants are highly concentrated with organic and inorganic pollutants that contain many toxics, mutagenics, carcinogenics and non-biodegradable aromatic compounds. The aforementioned drawbacks together with the ever increasing demands for the new chemicals have caused drastic perturbations in the ecosystem as well as serious health problems [1-3]. The Environmental Protection Agency (EPA) defines green policies and procedures for detecting and treating wastewaters based on ecosystem requirements that dictate the allowable level of water quality necessary to prevent health hazards. It is obvious for those working in the field that due to the toxicity and bio-refractory nature of such pollutants, conventional biochemical technologies would be of less effectiveness, or even in effective in resolving problems arising from this type of wastewaters. The degree of contamination of chemically polluted wastewaters depends mostly on the company production lines and formulations[4, 5]. Purification of waste water is a challenging topic. Miscellaneous ways have been proposed to purify wastewater, such as vacuum distillation and direct heating [6]. There are many types of companies such as polymer, pharmaceutical, food industries, power plants, oil refineries, natural gas processing, and biochemical factories which produce wastewaters possessing different types of contaminants under various operational parameters [7]. Accordingly, the efficacy or failure of a wastewater treatment process in removal of pollutants from the chemical company effluents depends considerably on the ability to identify which types of chemicals are...
contained in the waste and whether or not they can be detected. In this regards, combination of existing
approaches together with proper characterization techniques indeed provides useful insights [8-13]

In general, the conventional treatment processes fail to provide requirements needed for proper degradation of
influent materials; thus, secondary and/or tertiary treatments are inevitably essential for an efficient cleanup. For
instance, commonly used filtration methods by physical and/or chemical adsorption techniques are designed on
the basis of transferring the pollutant from one phase (liquid) to the other (solid) and, thus, suffer from the inability
to complete removal of contamination from the environment. On the other hand, photocatalytic treatment utilizing
semiconductors has always been in the way of development because of its superiority for degradation of pollutants
[14, 15]. In the course of photocatalysis, the oxidation is triggered by the attack of OH radicals having rate
constants of billions times higher than those rate constants expected from air as an oxidant [16-18]. Bearing in mind
the fact that efficient control of plants treating an influent by a universal control strategy would be a near-to-
impossible task, design of controllers capable of tracking fluctuations in the system at the course of treatment is of
vital importance[19].

There are some comprehensive studies that reveal the outstanding stability along with superior oxidative power of
titanium oxide (TiO\textsubscript{2}) as one of the best candidates to be considered as semiconductor photocatalyst for
environmental remediation and energy conversion processes [4, 5, 7]. Degradation of organic mixtures can be
catalyzed by radicals generated via gamma irradiation supported by TiO\textsubscript{2} catalysis effect. It is also possible that the
penetrated liquid wastes undergo degeneration because of a relatively high radiocatalysis efficiently [20].
Photocatalyst often exhibit suitable degradation in hydroxytrosol. Thus, its combination with solar light can boost
degradation rate through a multifaceted degradation mechanism [21]. Artificial light sources can provide adequate
ultraviolet (UV) radiation required for catalyst activation similar to what happens with sunlight. From the
economic perspective, however, industrial incentive policies to effectively use sunlight have been documented[22, 23]. For example, recent developments in the use of visible light for degradation has attracted more attention, for it
could considerably reduce the number of steps needed to guarantee an efficient degradation level[24, 25]. There is
enough evidence that single TiO\textsubscript{2} is solely responsible for the increase of electron-hole recombination rate, but
modification of TiO\textsubscript{2} will increase its efficiency. The use of co-adsorbents like active carbon, porous silica, and
kaolinite was also helpful in adsorbing the organic contaminants [18]. Application of SiO\textsubscript{2} as the membrane
between the γ-Fe\textsubscript{2}O\textsubscript{3} core and the TiO\textsubscript{2}shell was found to decline the influence of the γ-Fe\textsubscript{2}O\textsubscript{3} cores on the
TiO\textsubscript{2}photocatalytic activity, thereby a highly active and magnetically separable hybrid photocatalyst was obtained.

Despite the fact that all above-mentioned routes may intrinsically bring a number of beneficial advantageous, they
suffer from some shortcomings. The inability to detect and/or removal of unexpected contaminants in the
wastewater of real plants as well as the limited possibility of implementing control systems are the main
drawbacks to be addressed [19]. Further, the studied wastewaters have mostly been synthesized for research
purposes other than being sampled from the real plants. From a practical standpoint, it is believed that such
investigations encounter serious difficulties in the way of development and/or generalization of lab-scale results to
industrial cases. Removal of contaminants from the real-case chemical company wastewater was limitedly
addressed and discussed by the researchers among which the one performed in Bolivia can be specified [26]. In the
current research work, the capability and potential of photocatalytic methods to industrial wastewater treatment
from a local chemical company located at the northern area of Iran has been investigated. Considering the fact that
the effluent volume was indeed very high, the renewability of wastewater to be used in agricultural applications
was of critical importance. The complexity of analyzing the contaminants made us to evaluate the cleanup degree
based on chemical oxygen demand (COD) satisfying the level assigned to clean water according to EN 14049
irrigation techniques standard method. The reactor system was designed based upon operational and material
parameters, i.e., pH value, the amount of TiO\textsubscript{2}, H\textsubscript{2}O concentration and light intensity. Later, degradation
efficiency of photocatalytic treatment was studied and the results were compared with conventional wastewater
treatment, through which the best criterion satisfying the highest level of photocatalysis was specified and put into
practice.
2. Experimental Materials and Methods

2.1. Materials

The wastewater used was obtained from a commercial chemical company, located in the north of Iran, which produces lubricant oil. The main products manufactured by the company and the main components of each stream, which may exist in the effluent wastewater are summarized in Table 1. The typical characteristics of the influent wastewater used in this research work are reported in Table 2. Prior to treatment, the wastewater was diluted with distilled water to reach a COD value of 350 mg/L. This level of contamination was chosen based on open literature which enables comparison of the results of the present study based upon a real-case wastewater with those performed by others with chemically synthesized substrates.

\( \text{TiO}_2 \) (P-25, ca. 70% anatase –tetragonal form of \( \text{TiO}_2 \) usually found as brown crystals- and 30% rutile-lack or reddish-brown mineral of \( \text{TiO}_2 \)- with a BET surface area of 55.0 m\(^2\)/g and an average particle size of 30.0 nm was obtained from Degussa Co. (Germany). The chemicals such as H\(_2\)O\(_2\), NaOH, HCl, and diluents were all purchased in analytical grade from Merck Chemicals Co (Germany).

<table>
<thead>
<tr>
<th>Productions</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brake Oil</td>
<td>Diethylene glycol, Diethylene glycol monoethyl ether, Polyethylene glycol monobutyl ether, …</td>
</tr>
<tr>
<td>Brake Liquid</td>
<td>-</td>
</tr>
<tr>
<td>Gear Oil</td>
<td>Dithiocarbamate compound, ester of pentaerythritol, C12 to C20 fatty acid</td>
</tr>
<tr>
<td>Steering Oil</td>
<td>-</td>
</tr>
<tr>
<td>Hydraulic Oil</td>
<td>Glycol, Ester, Polyalphaolefine, Propylene glycol</td>
</tr>
<tr>
<td>Grease</td>
<td>Heavy fatty acids</td>
</tr>
<tr>
<td>Anti-Freeze &amp; Anti-Boil</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>Gasoline Additive</td>
<td>-</td>
</tr>
<tr>
<td>Glass Cleaner</td>
<td>Ethyl alcohol, Diethylene glycol mono butyl ether, cocamidopropyl betaine, copolymer polyvinyl pyrrolidone</td>
</tr>
<tr>
<td>Battery Water</td>
<td>Acid</td>
</tr>
<tr>
<td>Dashboard Spray</td>
<td>-</td>
</tr>
<tr>
<td>Hair &amp; Body Spray</td>
<td>-</td>
</tr>
<tr>
<td>Insecticide</td>
<td>Cypermethrine, Permethrine, Tetramethrine, Dialedrine</td>
</tr>
</tbody>
</table>

Table 1: Main products manufactured by the chemical company, which may form part of the wastewater.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Oil Factory Wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.9</td>
</tr>
<tr>
<td>Total Dissolved Solids (TDS)</td>
<td>3100</td>
</tr>
<tr>
<td>COD</td>
<td>3500</td>
</tr>
<tr>
<td>BOD</td>
<td>810</td>
</tr>
<tr>
<td>Total Organic Carbon (TOC)</td>
<td>1450</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>569</td>
</tr>
<tr>
<td>Oil &amp; Grease</td>
<td>1732</td>
</tr>
<tr>
<td>Fe</td>
<td>13.41</td>
</tr>
</tbody>
</table>

All values, except pH, are in mg/L.

2.2. Photocatalytic Treatment Experiments

Photocatalytic treatment was conducted in a batch reactor, whose schematic diagram is shown in Fig. 1. This small-scale reactor consisted in a cylindrical plexy-glass cell with 2.0 L capacity (80 mm i.d. and 400 mm height) and a UV-C lamp was placed in the center of the reactor. The reactor was filled with 0.7 L of chemical wastewater, Degussa TiO\(_2\): P-25 powders (0-4.0 g/L) and/or oxidant agent of H\(_2\)O\(_2\):(2.32–46.4 mM). The pH value of aqueous solution was adjusted by adding small amounts of 0.1 M NaOH or HCl. The suspended solution was stirred by an air spurger system to maintain aerobic conditions. All experiments, with or without H\(_2\)O\(_2\), were
carried out under similar operational conditions. Photocatalytic treatment was conducted up to 120 min and the liquid samples (10 mL) were withdrawn at time intervals of 15 min.

![Diagram of the photocatalytic reactor used in this research work.](image)

**FIG. 1. SCHEMATIC DIAGRAM OF THE PHOTOCATALYTIC REACTOR USED IN THIS RESEARCH WORK.**

2.3. Analytical Methods

Samples were taken periodically for analysis of COD through spectrophotometric measurements (ABFA 1998, Merck Co.). Prior to analysis, the samples were centrifuged (5000 rpm) for 15 min to precipitate the TiO$_2$ and removal of particles. Total Dissolved Solids (TDS), BOD, alkalinity and oil and grease contents in the wastewater were analyzed according to the Standard Methods (APHA, 2005).

3. Results and Discussion

The effectiveness and suitability of cleanup in this study could be expressed in terms of COD or degradation efficiency. Though both features are a measure of the relative oxygen-depletion effect of a waste contaminant, it is considered that the latter might in a better way visualize the nature of degradation [27].

3.1. Effect of TiO$_2$ Dosage on Photocatalytic Treatment Efficiency

As mentioned earlier, working on real-case wastewaters could to large extent reflect the complexity of analyzing the contaminants, in order to check the system capability of achieving a favorable cleanup degree. The presence of photocatalyst makes the photocatalytic degradation different from other advanced oxidation processes (AOPs) such as direct photolysis and the UV/H$_2$O$_2$ combination. In the selected method, the catalyst is the site where the reaction takes place and accelerates the production of H$_2$O$_2$ free radicals. Fig. 2 shows the effect of catalyst dosage on the photocatalytic degradation at 25°C and UV irradiation for an initial COD (COD$_o$) of 350 mg/L and pH of 7.0, using dosages in the range of 0.2 – 4 g/L and at different reaction times of 30 and 90 minutes.

As can be seen, the degradation efficiency increased by adding the catalyst up to 2.0 g/L, when it approached an optimum at the assigned value of catalyst dosage in the reactor configuration, followed by a descending trend at higher catalyst concentrations.

The maximum degradation efficiency was found to be 96% at the optimum concentration of 2.0 g/L and 90 min time. Previous researches indicated that the optimum amount of catalyst was 1.3 mg TiO$_2$/cm$^2$ in fixed bed systems, and 2.5 mg TiO$_2$/cm$^2$ in suspended systems [28, 29]. With regard to the reactor effective volume (700 mL), the optimum amount of catalyst in this geometry was nearby 1.75 g/L, which is very similar to what has been reported by Kulkarni [30]. It is well-known that increasing the concentration of catalyst will increase the number of active sites on photocatalyst surface, thereby the number of hydroxyl and superoxide radicals will be increased leading to enhanced degradation efficiency. The treatment of a chemical company wastewater with specified contamination level (COD of 350 mg/L) was performed in a photocatalytic reactor, where the effects of catalyst loading, initial solution
pH, inorganic oxidative concentration, light intensity and time of reaction on the photodegradation rate and treatment efficiency were studied. Investigations in virtue of degradation efficiency and final COD values revealed that the optimum catalyst amount was about 2.0 g/L while the optimum pH value was approximately nearby 7.0. The results also confirmed that by simultaneous use of H\textsubscript{2}O\textsubscript{2}, TiO\textsubscript{2}, and UV the efficiency of photocatalytic degradation will be improved. Increasing light intensity had a positive effect on photo-degradation and improved the rate of reaction. Finally, this research showed that the photo-degradation rate speed up in the presence of catalyst and, therefore, the positive effect of catalyst was stronger than the negative shading effect until the optimum amount of catalyst is reached. From the perspective of environment, the cleaned wastewater sampled from industrial unit can be reused for irrigation purposes because the level of contamination after treatment has been fallen into the region satisfying cleanup degree defined by the Jordan standard.

\textbf{It can be obviously seen that the ultimate contamination level corresponding to the assigned combined treatment method (H\textsubscript{2}O\textsubscript{2}/TiO\textsubscript{2}/UV) during 90 minutes takes COD values below 50 mg/L (approximately with seven-fold decrease when compared with initial value of 350 mg/L), which can be considered for both unrestricted irrigation (maximum allowed COD equivalent to 100 mg/L) from soil, flora, hydrological and public health and somewhat lower than the maximum allowable level (70 mg/L) for discharge to river. The results of this investigation suggest that an adequate combination of H\textsubscript{2}O\textsubscript{2}, TiO\textsubscript{2}, and UV as well as of exposure time will allow enhancing the efficiency of photocatalytic degradation. Nevertheless, according to Jordan Standard (JS #893) of the year 1995 for treated wastewater disposal, the COD values of around 200 situate in the safe area for irrigation [43]. Since the COD value corresponding to clean water for irrigation purposes is of critical importance, the dependency of this criterion on the time of photocatalytic degradation is also depicted in Fig. 8.}

The H\textsubscript{2}O\textsubscript{2}/TiO\textsubscript{2}/UV system achieved a nearly two-fold increase of the reaction rate compared to the TiO\textsubscript{2}/UV system. This can be explained in this manner that decomposition is mainly controlled by the hydroxyl radicals produced in the presence of H\textsubscript{2}O\textsubscript{2} in the H\textsubscript{2}O\textsubscript{2}/TiO\textsubscript{2}/UV system [41, 42]. H\textsubscript{2}O\textsubscript{2} and b) formation of an intermediate component which decreases the degradation rate according to the shading effect of catalyst and intermediates. A Langmuir–Hinshelwood kinetic equation type is adopted to describe the substrate concentration effect on its photodegradation rate [38-40]. Table 3 summarizes the apparent rate constant \( k_{app} \) values and the determination.

\textbf{Fig. 7 shows the effect of degradation time on treatment efficiency in photocatalytic process. In direct photolysis with 15-W UV-C alone, the maximum efficiency achieved was 86% at 120 min, while by adding 2.32mM H\textsubscript{2}O\textsubscript{2} the degradation efficiency increased to 92%. A efficiency of 89% was obtained when 0.5g/L of TiO\textsubscript{2} was added to the}
solution and treated under 15-W UV-C irradiation. Finally, the combination of the last processes (2.32mM H₂O₂, 0.5 g/L TiO₂, and 15-W UV-C system) improved organic matter removal up to 97%. To explain this phenomenon, there are two parameters to take into account, which affect this process; a) Intensified ‘OH radical generation due to incorporation of TiO₂ and

A plot of \(-\ln(C/C₀)\) versus reaction time \(t\) yields a straight line, whose slope coincides with the apparent rate constant. Fig. 6 shows the change of the apparent rate coefficient (\(k_{app}\)) for different light intensities studied. The linear (upward) dependence of rate coefficient on the UV light intensity from UV-A 15 W (0.01 min⁻¹) to UV-C 30 W (0.025 min⁻¹) indicates the significance of UV light intensity in such photodegradation process for organic matter. This, from the other side, reflects the reliability of degradation analysis in virtue of the COD criterion.

where \(k\) is the inherent rate constant and \(K\) is the Langmuir adsorption constant. When the adsorption is partly weak and/or the concentration of organic compound is low, Eq. (4) can be simplified to the first-order kinetics with an apparent rate constant \(k_{app}\), as follows:

As illustrated, an increase in the light intensity from 15.0 to 30.0 W caused an increase in the degradation efficiency from 60% to 83% at 90 min and from 70% to 97% at 120 min. It can be stated that by increasing the light intensity, the reaction rate has been increased due to an enhanced generation rate of H₂O₂ radicals against photo decomposition of H₂O₂ [38]. Moreover, the effect of different UV wave lengths (15-W UV-A, UV-B and UV-C light) showed that the degradation efficiency of wastewater increased by increasing the power of light photon from wave length of UV-A (60%) to UV-B (69%) and to UV-C (73%) within 90 min time. The Langmuir–Hinshelwood model is generally used to describe the kinetics of photocatalytic reactions of aquatic organics [4]. The relationship between degradation rate (\(r\)) and the concentration of organic compound (\(C\)) is given as follows:

Fig. 5 shows the effect of light intensity on the efficiency of photocatalytic degradation.

Although, due to complexity of the selected wastewater, the intensity and/or occurrence of such reactions needs further investigations, the trend observed showed a progressive increase in the degradation efficiency at H₂O₂ concentrations at least up to a H₂O₂ concentration of 11.6mM.

These functions inhibit the electron-hole recombination at the semiconductor surface according to the following equations [27, 35-37]:

H₂O₂, as an inorganic oxidant, has an impressive role in AOPs. In this experiment, the effect of additional H₂O₂ concentration on photodegradation of chemical wastewater was also studied. The variation of the degradation efficiency for the different H₂O₂ concentrations studied in the range of 2.32-46.4 mM is plotted in Fig. 4. As can be observed by increasing the H₂O₂ concentrations from 2.32mM to11.6mM and then to 46.4mM, the degradation efficiency increased from74% to 95% and then to96% respectively at a reaction time of 90 min. It can also be simply seen that the treatment time has serious impact on the degradation efficiency, where the time of 30 min was not sufficient to achieve a complete degradation even at very high concentrations of H₂O₂. This suggests that the photodegradation underwent situations that might be of interest to be understood. There is some evidences that the reactive radical intermediates (‘OH), formed from these oxidants, react with the photogenerated electrons and fulfill a dual function: a) as strong oxidant and b) as electron scavengers.

From this perspective, different behavioral situations were reported mostly concerning with substrates synthesized in the lab not sampled from chemical company wastewaters.

The pH plays an important role in the photocatalytic reactions occurring on the surface and determines the surface charge properties of photocatalyst and size of solution aggregates [31]. While some compounds are uncharged at common pH conditions of natural water or wastewater, some other compounds could exhibit a wide variation in speciation (or charge) and physico-chemical properties. Moreover, there are some compounds, which can exist in positive, neutral and negative forms in aqueous solution, which can significantly influence the photocatalyst treatment behavior [4]. The recent research on TiO₂ points of zero charge (pzc) by Kosmulski and coworkers indicated that the TiO₂ used in the present research(Degussa P-25, 80% anatase and 20% rutile) has a pzc of 6.9 [32]. Fig. 3 shows the effect of pH on photo-degradation percentage. As can be seen in this figure, by increasing the pH
from 4.0, the treatment efficiency increased until achieving a maximum value of 79% at a pH value of 6.5. Since the lower degradation percentage was not much smaller compared to the maximum value reached at a pH of 6.5 (near 13% difference between maximum and minimum degradation percentage) then, the influence of solution pH on photocatalytic degradation proved to be less important compared to the other parameters. Therefore, for all experiments the neutral pH of 7.0 was used.

The reason for efficiency decrease at high dosages may be attributed to some limiting phenomena such as light scattering by more TiO$_2$ catalyst within the reaction medium (interception of the light by excess catalyst). Since the excess catalyst prevents the illumination of •OH radicals, the primary oxidant in the photocatalytic system will be decreased, thereby the efficiency of the degradation reduced accordingly. Moreover, a rise in the catalyst concentration over the optimum dosage may result in the congestion of catalyst particles, which causes partially the catalyst surface becoming unusable for photon absorption [22, 28-30].

3.2. Effect of pH on Photocatalytic Treatment Efficiency

The pH plays an important role in the photocatalytic reactions occurring on the surface and determines the surface charge properties of photocatalyst and size of solution aggregates [31]. While some compounds are uncharged at common pH conditions of natural water or wastewater, some other compounds could exhibit a wide variation in speciation (or charge) and physico-chemical properties. Moreover, there are some compounds, which can exist in positive, neutral and negative forms in aqueous solution, which can significantly influence the photocatalyst treatment behavior [4]. The recent research on TiO$_2$ points of zero charge (pzc) by Kosmulski and coworkers indicated that the TiO$_2$ used in the present research (Degussa P-25, 80% anatase and 20% rutile) has a pzc of 6.9 [32]. Fig. 3 shows the effect of pH on photo-degradation percentage. As can be seen in this figure, by increasing the pH from 4.0, the treatment efficiency increased until achieving a maximum value of 79% at a pH value of 6.5. Since the lower degradation percentage was not much smaller compared to the maximum value reached at a pH of 6.5 (near 13% difference between maximum and minimum degradation percentage) then, the influence of solution pH on photocatalytic degradation proved to be less important compared to the other parameters. Therefore, for all experiments the neutral pH of 7.0 was used. The treatment of a chemical company wastewater with specified contamination level (COD of 350 mg/L) was performed in a photocatalytic reactor, where the effects of catalyst loading, initial solution pH, inorganic oxidative concentration, light intensity and time of reaction on the photodegradation rate and treatment efficiency were studied. Investigations in virtue of degradation efficiency and final COD values revealed that the optimum catalyst amount was about 2.0 g/L while the optimum pH value was approximately nearby 7.0. The results also confirmed that by simultaneous use of H$_2$O$_2$, TiO$_2$, and UV the efficiency of photocatalytic degradation will be improved. Increasing light intensity had a positive effect on photodegradation and improved the rate of reaction. Finally, this research showed that the photo-degradation rate speed up in the presence of catalyst and, therefore, the positive effect of catalyst was stronger than the negative shading effect until the optimum amount of catalyst is reached. From the perspective of environment, the cleaned wastewater sampled from industrial unit can be reused for irrigation purposes because the level of contamination after treatment has been fallen into the region satisfying cleanup degree defined by the Jordan standard.

It can be obviously seen that the ultimate contamination level corresponding to the assigned combined treatment method (H$_2$O$_2$/TiO$_2$/UV) during 90 minutes takes COD values below 50 mg/L (approximately with seven-fold decrease when compared with initial value of 350 mg/L), which can be considered for both unrestricted irrigation (maximum allowed COD equivalent to 100 mg/L) from soil, flora, hydrological and public health and somewhat lower than the maximum allowable level (70 mg/L) for discharge to river. The results of this investigation suggest...
that an adequate combination of H$_2$O$_2$, TiO$_2$, and UV as well as of exposure time will allow enhancing the efficiency of photocatalytic degradation. Nevertheless, according to Jordan Standard (JS #893) of the year 1995 for treated wastewater disposal, the COD values of around 200 situate in the safe area for irrigation [43].

Since the COD value corresponding to clean water for irrigation purposes is of critical importance, the dependency of this criterion on the time of photocatalytic degradation is also depicted in Fig. 8.

The H$_2$O$_2$/TiO$_2$/UV system achieved a nearly two-fold increase of the reaction rate compared to the TiO$_2$/UV system. This can be explained in this manner that decomposition is mainly controlled by the hydroxyl radicals produced in the presence of H$_2$O$_2$ in the H$_2$O$_2$/TiO$_2$/UV system [41, 42].

H$_2$O$_2$: and b) formation of an intermediate component which decreases the degradation rate according to the shading effect of catalyst and intermediates. A Langmuir–Hinshelwood kinetic equation type is adopted to describe the substrate concentration effect on its photodegradation rate [38-40]. Table 3 summarizes the apparent rate constant $k_{app}$ values and the determination.

Fig. 7 shows the effect of degradation time on treatment efficiency in photocatalytic process. In direct photolysis with 15-W UV-C alone, the maximum efficiency achieved was 86% at 120 min, while by adding 2.32mM H$_2$O$_2$ the degradation efficiency increased to 92%. A efficiency of 89% was obtained when 0.5g/L of TiO$_2$ was added to the solution and treated under 15-W UV-C irradiation. Finally, the combination of the last processes (2.32mM H$_2$O$_2$, 0.5 g/L TiO$_2$, and 15-W UV-C system) improved organic matter removal up to 97%. To explain this phenomenon, there are two parameters to take into account, which affect this process; a) Intensified ´OH radical generation due to incorporation of TiO$_2$ and

A plot of $-\ln(C/C_0)$ versus reaction time $t$ yields a straight line, whose slope coincides with the apparent rate constant. Fig. 6 shows the change of the apparent rate coefficient ($k_{app}$) for different light intensities studied. The linear (upward) dependence of rate coefficient on the UV light intensity from UV-A 15 W (0.01 min$^{-1}$) to UV-C 30 W (0.025 min$^{-1}$) indicates the significance of UV light intensity in such photodegradation process for organic matter. This, from the other side, reflects the reliability of degradation analysis in virtue of the COD criterion.

where $k$ is the inherent rate constant and $K$ is the Langmuir adsorption constant. When the adsorption is partly weak and/or the concentration of organic compound is low, Eq. (4) can be simplified to the first-order kinetics with an apparent rate constant $k_{app}$, as follows:

As illustrated, an increase in the light intensity from 15.0 to 30.0 W caused an increase in the degradation efficiency from 60% to 83% at 90 min and from 70% to 97% at 120 min. It can be stated that by increasing the light intensity, the reaction rate has been increased due to an enhanced generation rate of H$_2$O$_2$: radicals against photo decomposition of H$_2$O$_2$: [38]. Moreover, the effect of different UV wave lengths (15-W UV-A, UV-B and UV-C light) showed that the degradation efficiency of wastewater increased by increasing the power of light photon from wave length of UV-A (60%) to UV-B (69%) and to UV-C (73%) within 90 min time. The Langmuir–Hinshelwood model is generally used to describe the kinetics of photocatalytic reactions of aquatic organics [4]. The relationship between degradation rate ($r$) and the concentration of organic compound (C) is given as follows:

Fig. 5 shows the effect of light intensity on the efficiency of photocatalytic degradation.

Although, due to complexity of the selected wastewater, the intensity and/or occurrence of such reactions needs further investigations, the trend observed showed a progressive increase in the degradation efficiency at H$_2$O$_2$: concentrations at least up to a H$_2$O$_2$: concentration of 11.6mM.

These functions inhibit the electron-hole recombination at the semiconductor surface according to the following equations [27, 35-37]:

H$_2$O$_2$: as an inorganic oxidant, has an impressive role in AOPs. In this experiment, the effect of additional H$_2$O$_2$: concentration on photodegradation of chemical wastewater was also studied. The variation of the degradation efficiency for the different H$_2$O$_2$: concentrations studied in the range of 2.32-46.4 mM is plotted in Fig. 4. As can be observed by increasing the H$_2$O$_2$: concentrations from 2.32mM to11.6mM and then to 46.4mM, the degradation
efficiency increased from 74% to 95% and then to 96% respectively at a reaction time of 90 min. It can also be simply seen that the treatment time has serious impact on the degradation efficiency, where the time of 30 min was not sufficient to achieve a complete degradation even at very high concentrations of H₂O₂. This suggests that the photodegradation underwent situations that might be of interest to be understood. There is some evidences that the reactive radical intermediates (ºOH), formed from these oxidants, react with the photogenerated electrons and fulfill a dual function: a) as strong oxidant and b) as electron scavengers.

From this perspective, different behavioral situations were reported mostly concerning with substrates synthesized in the lab not sampled from chemical company wastewaters.

It is to be mentioned that the degradation behavior against pH value depends strongly on the nature and concentration of the substrate [33, 34]. From this perspective, different behavioral situations were reported mostly concerning with substrates synthesized in the lab not sampled from chemical company wastewaters.

**3.3. Effect of H₂O₂ Concentration on Photocatalytic Treatment Efficiency**

H₂O₂, as an inorganic oxidant, has an impressive role in AOPs. In this experiment, the effect of additional H₂O₂ concentration on photodegradation of chemical wastewater was also studied. The variation of the degradation efficiency for the different H₂O₂ concentrations studied in the range of 2.32-46.4 mM is plotted in Fig. 4. As can be observed by increasing the H₂O₂ concentrations from 2.32mM to 11.6mM and then to 46.4mM, the degradation efficiency increased from 74% to 95% and then to 96% respectively at a reaction time of 90 min. It can also be simply seen that the treatment time has serious impact on the degradation efficiency, where the time of 30 min was not sufficient to achieve a complete degradation even at very high concentrations of H₂O₂. This suggests that the photodegradation underwent situations that might be of interest to be understood. There is some evidences that the reactive radical intermediates (ºOH), formed from these oxidants, react with the photogenerated electrons and fulfill a dual function: a) as strong oxidant and b) as electron scavengers.

**Fig. 3. Effect of pH on treatment efficiency by photocatalytic method at 25°C (Temp: 25°C, COD₀ = 350 mg/L, 1.0 g/L TiO₂, and reaction time of 90 min).**

**Fig. 4. Effect of the H₂O₂ concentration on treatment efficiency by photocatalytic method using H₂O₂/UV process (Temp: 25°C, COD₀ = 350 mg/L, pH 7.0).**
These functions inhibit the electron-hole recombination at the semiconductor surface according to the following equations [27, 35-37]:

\[ H_2O_2 + O_2 \rightarrow \cdot OH + OH^- + O_2 \]  
\[ H_2O_2 + h\nu \rightarrow 2\cdot OH \]  
\[ H_2O_2 + e_{CB} \rightarrow \cdot OH + OH^- \]

Although, due to complexity of the selected wastewater, the intensity and/or occurrence of such reactions needs further investigations, the trend observed showed a progressive increase in the degradation efficiency at \( \text{H}_2\text{O}_2 \) concentrations at least up to a \( \text{H}_2\text{O}_2 \) concentration of 11.6mM.

3.4. Effect of Light Intensity on Photocatalytic Treatment Efficiency

Fig. 5 shows the effect of light intensity on the efficiency of photocatalytic degradation.

![Fig. 5. Effect of light intensity on treatment efficiency by photocatalytic method (Temp. 25 ºC, COD0 = 350 mg/L, 1.0 g/L TiO2, pH 7.0 and reaction time of 90 min).](image)

As illustrated, an increase in the light intensity from 15.0 to 30.0 W caused an increase in the degradation efficiency from 60% to 83% at 90 min and from 70% to 97% at 120 min. It can be stated that by increasing the light intensity, the reaction rate has been increased due to an enhanced generation rate of \( \text{H}_2\text{O}_2 \) radicals against photo decomposition of \( \text{H}_2\text{O}_2 \) [38]. Moreover, the effect of different UV wave lengths (15-W UV-A, UV-B and UV-C light) showed that the degradation efficiency of wastewater increased by increasing the power of light photon from wave length of UV-A (60%) to UV-B (69%) and to UV-C (73%) within 90 min time. The Langmuir–Hinshelwood model is generally used to describe the kinetics of photocatalytic reactions of aquatic organics [4]. The relationship between degradation rate \( (r) \) and the concentration of organic compound \( (C) \) is given as follows:

\[ r = -\frac{dC}{dt} = \frac{k_r KC}{1 + KC} \]  

where \( k_r \) is the inherent rate constant and \( K \) is the Langmuir adsorption constant. When the adsorption is partly weak and/or the concentration of organic compound is low, Eq. (4) can be simplified to the first-order kinetics with an apparent rate constant \( k_{app} \), as follows:

\[ \ln\left(\frac{C}{C_0}\right) = -k_r K t = -k_{app} t \]

A plot of \(-\ln(C/C_0)\) versus reaction time \( t \) yields a straight line, whose slope coincides with the apparent rate constant. Fig. 6 shows the change of the apparent rate coefficient \( (k_{app}) \) for different light intensities studied. The linear (upward) dependence of rate coefficient on the UV light intensity from UV-A 15 W (0.01 min\(^{-1}\)) to UV-C 30 W
(0.025 min\(^{-1}\)) indicates the significance of UV light intensity in such photodegradation process for organic matter. This, from the other side, reflects the reliability of degradation analysis in virtue of the COD criterion.

3.5. Effect of Time Process on Photocatalytic Treatment Efficiency

Fig. 7 shows the effect of degradation time on treatment efficiency in photocatalytic process. In direct photolysis with 15-W UV-C alone, the maximum efficiency achieved was 86% at 120 min, while by adding 2.32mM H\(_2\)O\(_2\) the degradation efficiency increased to 92%. A efficiency of 89% was obtained when 0.5g/L of TiO\(_2\) was added to the solution and treated under 15-W UV-C irradiation. Finally, the combination of the last processes (2.32mM H\(_2\)O\(_2\), 0.5 g/L TiO\(_2\), and 15-W UV-C system) improved organic matter removal up to 97%. To explain this phenomenon, there are two parameters to take into account, which affect this process; a) Intensified \(^{1}\)OH radical generation due to incorporation of TiO\(_2\) and H\(_2\)O\(_2\) and b) formation of an intermediate component which decreases the degradation rate according to the shading effect of catalyst and intermediates. A Langmuir–Hinshelwood kinetic equation type is adopted to describe the substrate concentration effect on its photodegradation rate [38-40]. Table 3 summarizes the apparent rate constant \(k_{\text{app}}\) values and the determination coefficients obtained for different wastewater treatment systems operating with different conditions.
### Table 3. The change of rate constant for the different treatments and operation conditions tested.

<table>
<thead>
<tr>
<th>System</th>
<th>$k_{app}$ (min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>$1.41 \times 10^{-3}$</td>
<td>0.9956</td>
</tr>
<tr>
<td>UV + 2.32 mM H$_2$O$_2$</td>
<td>$1.52 \times 10^{-3}$</td>
<td>0.9871</td>
</tr>
<tr>
<td>UV + 0.5 g/L TiO$_2$</td>
<td>$1.48 \times 10^{-3}$</td>
<td>0.9743</td>
</tr>
<tr>
<td>UV + 2.32 mM H$_2$O$_2$ + 0.5 g/L TiO$_2$</td>
<td>$2.72 \times 10^{-3}$</td>
<td>0.9786</td>
</tr>
</tbody>
</table>

The H$_2$O$_2$/TiO$_2$/UV system achieved a nearly two-fold increase of the reaction rate compared to the TiO$_2$/UV system. This can be explained in this manner that decomposition is mainly controlled by the hydroxyl radicals produced in the presence of H$_2$O$_2$ in the H$_2$O$_2$/TiO$_2$/UV system [41, 42].

Since the COD value corresponding to clean water for irrigation purposes is of critical importance, the dependency of this criterion on the time of photocatalytic degradation is also depicted in Fig. 8.

![Figure 8](image_url)

**Fig. 8. Variation of the COD of treated wastewater as a function of photocatalysis time (Temp. 25 °C, COD$_0$ = 350 mg/L, pH 7.0 and different oxidation and catalyst conditions).**

It can be obviously seen that the ultimate contamination level corresponding to the assigned combined treatment method (H$_2$O$_2$/TiO$_2$/UV) during 90 minutes takes COD values below 50 mg/L (approximately with seven-fold decrease when compared with initial value of 350 mg/L), which can be considered for both unrestricted irrigation (maximum allowed COD equivalent to 100 mg/L) from soil, flora, hydrological and public health and somewhat lower than the maximum allowable level (70 mg/L) for discharge to river. The results of this investigation suggest that an adequate combination of H$_2$O$_2$, TiO$_2$, and UV as well as of exposure time will allow enhancing the efficiency of photocatalytic degradation. Nevertheless, according to Jordan Standard (JS #893) of the year 1995 for treated wastewater disposal, the COD values of around 200 situate in the safe area for irrigation [43].

### 4. Conclusions

The treatment of a chemical company wastewater with specified contamination level (COD of 350 mg/L) was performed in a photocatalytic reactor, where the effects of catalyst loading, initial solution pH, inorganic oxidative concentration, light intensity and time of reaction on the photodegradation rate and treatment efficiency were studied. Investigations in virtue of degradation efficiency and final COD values revealed that the optimum catalyst amount was about 2.0 g/L while the optimum pH value was approximately nearby 7.0. The results also confirmed that by simultaneous use of H$_2$O$_2$, TiO$_2$, and UV the efficiency of photocatalytic degradation will be improved. Increasing light intensity had a positive effect on photo-degradation and improved the rate of reaction. Finally, this research showed that the photo-degradation rate speed up in the presence of catalyst and, therefore, the positive effect of catalyst was stronger than the negative shading effect until the optimum amount of catalyst is reached. From the perspective of environment, the cleaned wastewater sampled from industrial unit can be reused for
irrigation purposes because the level of contamination after treatment has been fallen into the region satisfying cleanup degree defined by the Jordan standard.

**Reference**


