Solar Photocatalytic Detoxification Using Nano particles of Titanium Oxide: A Treatment Method for Actual Decentralized wastewater unit Effluents

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Abstract

The solar photocatalytic oxidation of potassium hydrogen phthalate (KHP) was examined in a batch reactor as a model. Catalyst load, initial KHP concentration and pH are variables studied in this research. The kinetics model for the reaction was investigated in this study. The nano particle of TiO₂ (P25) used as catalyst for this reaction. The results revealed that the optimum catalyst load in the batch reactor is 1g/L of TiO₂. The removal efficiency of the organic compounds reduces as the initial concentration increases, with a first order reaction rate at high concentration and zero order reaction rate at low concentrations were noticed in the study. The zero order at low concentrations reaction has a rate constant of 23.53 mg L⁻¹ h⁻¹, while high concentrations the first order has a rate constant of 0.6225 h⁻¹. The photocatalytic oxidation is dependent on pH and, it increases with the increasing of pH. Treatment of secondary treated wastewater results in about 50% removal of organic matter and 100% inactivation of E-Coli with no regrowth after 24h storage in dark was obtained.

Keywords: wastewater treatment, Catalytic degradation, TiO₂, P25/Evonic, photo catalytic ; water treatment KHP degradation; TiO₂ Detoxification; solar radiation; TiO₂ kinetics
1. Introduction

Degradation by solar photocatalysis using titanium oxide has been proposed as a viable process to detoxify wastewater. During last decades, many researchers have shown that many pesticides, herbicides, surfactants, dyes pharmaceuticals and personal care products may completely oxidize into non-toxic compounds.

As residual pesticides in drinking water threaten human health, removal of these compounds is a priority. Titanium oxide, suspended and immobilized, proved to be efficient in oxidizing different pesticides. Senthilnathan & Philip (2009) examined the elimination of Lindane, methyl parathion and dichlorvos. The degradation rate of pesticides compared in both suspended and immobilized TiO$_2$ systems, and for single and mixed pesticides where titanium oxide removed the pesticides efficiently, and that the degradation pattern of mixed pesticides was not similar to that of single pesticide. Ahmed et al, (2011) studied the effect of different operating conditions on the photocatalytic degradation of pesticides and phenols. Results reported that the photocatalytic degradation of organic compounds varies with the type of photocatalyst and composition, light intensity, initial concentration of pesticide or phenol compound, load of the catalyst, pH of the reaction medium, ionic components in water, solvent types, oxidizing agents/electron acceptors, catalyst application method, and calcinations temperature in water environment.

Pharmaceutical compounds are also significant pollutants in wastewater and particular consideration should be given to the medicines which are available without prescription which include non-steroidal painkillers and anti-inflammatory drugs. Remediation by photocatalytic degradation seems to be promising. Klavarioti et al, (2009) assessed the efficiency of various AOPs for pharmaceutical removal from aqueous systems. Radjenović et al, (2009) studied the feasibility and performance of photocatalytic degradation of anti-inflammatory drug acetaminophen and β-blocker atenolol in a pilot-plant scale Compound Parabolic Collectors (CPCs) under natural illumination. Total disappearance of the original compounds and discreet mineralization have attained in all experiments. Czech and Rubinowska, (2013) studied the photocatalytic oxidation of diclofenac, metoprolol, estrone and chloramphenicol was carried out in the tube reactor using different commercially available TiO$_2$. It was noted that generally
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anatase TiO$_2$ is the most active in the photocatalytic oxidation of diclofenac, chloramphenicol and estrone, while the presence of rutile TiO$_2$ improved the photooxidation of metoprolol.

Most of the research studies using titanium oxide as a photocatalyst oriented towards dyes removal, since dyes are widely used in industry, thereby they are discharged in wastewater. AOPs recently applied for the destructive of dyes in wastewater rather than transfer of these compounds to the sludge. Ram et al, (2012) studied the degradation of commercial reactive Procion Yellow dye using photocatalyst combinations (TiO$_2$/UV/Solar/pH). The results indicated 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).

Further work, where the effect of chemical structure on photocatalysis efficiency was investigated by Khataeea et al, (2009), they studied the removal of (Acid Orange 10, Acid Orange 12 and Acid Orange 8) with different structure and different substitute groups using supported TiO$_2$ photocatalyst under UV light irradiation. The dye solutions could be completely decolorized and effectively mineralized, with an average overall TOC removal larger than 94% for a photocatalytic reaction time reached 6 hours.

Olive mill wastewater (OMW) is heavily polluted and cannot be disposed without proper treatment such as biological treatment. Phenolic compounds are considered serious problems with OMW due to their recalcitrance and strong brown to dark color. Costa and Alves, (2013) investigated post-treatment of anaerobic digested OMW using photocatalytic reactor with UV and immobilized TiO$_2$. The results showed that phenols and color were completely removed after 24h of treatment, while the COD removal was partial. El Hajjouji et al, (2008) also found that the COD, coloration at 330 nm and the level of phenols in OMW decreases by 22%, 57% and 94% respectively after 24 h photocatalysis treatment using TiO$_2$ under UV irradiation. The differences between these three values indicate the persistence of colorless, non-phenolic compounds.

The implementation of photocatalyst for municipal wastewater treatment indicated that significant removal of organic pollutants and the inactivation of fecal bacteria were close to 100% (Bernabeu, et al, 2011). Photocatalytic disinfection of secondary treated wastewater was studied where total coliform and enterococci activities were investigated against three types of titanium oxide under UV-A irradiation. The results showed that TiO$_2$ (Degussa P25) was the most effective catalyst, and enterococci showed a stronger resistance to disinfection by the
photocatalysis (Alena, and Sahu, 2013). Although disinfection of wastewater by solar UV only was subject to some projects, solar water disinfection (SODIS method) showed an improve in people health with no access to safe drinking water through a number of SODIS projects around the world.

Disinfection of surface water samples to be potable water carried out in comparison with distilled water to investigate the inactivation rates of Escherichia coli using immobilized nanoparticle TiO₂ films (Alrousan, et al, 2009). The results found indicate that humic acid significantly decreased the disinfection rate of Escherichia coli, while pH has not. Nitrate and sulfate spiked into distilled water also decreased the disinfection rate.

Ong et al, (2009) had explored photodegradation of Congo Red and Reactive Yellow2 using immobilized TiO₂. The photocatalytic degradation of both dyes was investigated under sun irradiation. The findings showed that the percentage of dye removal increased with decreased initial concentration and increasing irradiation time.

Although fundamental and engineering researches have established the solar photocatalysis technology in wastewater treatment, the industrial application is still in a nascent stage and there are challenges that need to be overcome, such as the solar utilization efficiency, the construction and operation of photoreactor, and the separation of the photocatalysts (Zhang, and Zhang, 2014).

This study aims at applying this promising technology for the remediation of real treated wastewater (collected from a local septic tank) in an efficient and affordable way for the potential users of treated wastewater at homes, small institutions, hotels and small industries such as pharmaceuticals manufacturing factories, food processing plants, and textile and paper industries. In addition the study objective is also to investigate the detoxification of treated wastewater as a tertiary treatment by photocatalysis. This process will be a great help to local rural people where wastewater treatment plant and water grid does not exist.

Methodology and materials

To conduct the experimental work, it is firstly advised to start with one component to investigate the oxidation effects of nano-particles TiO₂ P25, on the degradation process as a
model rather than a matrix of organic and inorganic compounds. Therefore, Potassium Hydrogen Phthalate (KHP) was chosen to be the model compound for this study, since this compound is used as a standard for both chemical oxygen demand (COD) and total organic carbon (TOC). The optimum conditions resulted for KHP will subsequently apply to detoxification of the real wastewater effluent. The decentralized wastewater treatment unit sued in this investigation was constructed and built through fund from German Federal Ministry of Education and Research (BMBF), under the name of SMART (Sustainable Management of Available Water Resources with Innovative Technologies, http://smart.bau.edu.jo/index.html).

Chemical oxygen demand set here to be the indicator parameter of degradation process, because it is a colligative property that measures all carbonaceous compounds within the sample. Thus when total mineralization occurs a zero value of COD will be attained, while incomplete mineralization will produce intermediate compounds which will be characterized by a COD value, and this is in contrary with identification of certain compound.

AEROXIDE® TiO$_2$ P25, kindly donated by Evonik, is the photocatalyst used in this study. The main characteristics of the photocatalyst are summarized in Table 1.

**Table 1. Main properties of AEROXIDE® TiO$_2$ P25**

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (BET) m$^2$/g</td>
<td>50 ± 15</td>
</tr>
<tr>
<td>Average primary particle size nm</td>
<td>21</td>
</tr>
<tr>
<td>Tapped density (approx. value) g/l acc. to DIN EN ISO 787/11, Aug. 1983</td>
<td>approx. 130</td>
</tr>
<tr>
<td>Titanium dioxide based on ignited material wt.%</td>
<td>&gt; 99.50</td>
</tr>
</tbody>
</table>

Source: [www.aerosil.com](http://www.aerosil.com)

**Batch experimental work**
The lab scale experiments were simply performed in one liter Pyrex beaker, to let the direct sun irradiation enter through it, with continuous stirring of nano-particles TiO$_2$ and the solution of interest, representing continuous stirring tank reactor, under artificial or solar radiation. A mere mixing is sufficient to introduce oxygen to the reactor. This type of reactor provides a large surface area between the reactant and catalyst.

Synthetic potassium hydrogen Phthalate (KHP) with different concentrations of known COD were prepared and set as water samples. The addition of KHP to deionized water results in pH drop to about 4, therefore pH adjustment to the required value was an essential step for each preparation. To find out the optimum catalyst dose, different TiO$_2$ doses were added (0.25g, 0.5g, 1g, 2g) to the batch reactors that contain 300mg/l COD of KHP solution at pH 7. All experiments run for 9 hours under solar radiation –all experimental works have conducted under direct sun irradiation during the period of June-September on the roof of the faculty of Agriculture Technology of Al-Balqa applied university- . Samples for analyses were taken every hour. COD analyzed for each sample. Solar radiation intensity measured by SPER SCIENTIFIC 850009, and the readings were recorded for each experiment.

Once the optimum dose of TiO$_2$ was obtained, the effect of the initial COD concentration was studied by running different initial COD values (50, 100, 300 mg/l) at pH 7 and at the optimum dose of TiO$_2$ for 9 hours under solar radiation again. Samples were taken every hour and COD was analyzed.

Since pH has a great influence on the degradation process, its effect studied by running the experiment at the optimum conditions of TiO$_2$ dose and optimum COD concentration for different initial pH values. Once the optimum operating conditions were set for KHP solution, real secondary treated wastewater samples were collected from the SMART project unit in rural area located near by the university campus, and investigated under these same conditions.

Secondary treated wastewater samples analyzed for pH, EC, major cations and anions, COD, BOD, total coliform and E-coli. These wastewater samples were treated by powdered TiO$_2$ in the batch reactor for 8 hours under solar radiation at the optimum dose of TiO$_2$ and pH value, and analyzed for COD. While E-coli analyzed each two hours. Control samples of KHP solution
and wastewater in the absence of TiO\textsubscript{2} will run under the same conditions to confirm the solely photocatalytic reaction.

**Results and Discussion**

1. **Effect of TiO\textsubscript{2} dose on KHP degradation**

TiO\textsubscript{2} at low dose can result in a surface site limiting reaction and insufficient radical generation, whereas a high TiO\textsubscript{2} dose can reduce the transmittance of the UV light. Therefore, four doses of TiO\textsubscript{2} at pH 7 were carried out to find the optimum dose, that is, the dose with the highest removal of KHP from the solution measured as COD and high transmittance radiation of UVA and UVB type with an intensity of 12-15 mW/cm\textsuperscript{2} as shown in Fig. 1- a and 1-b. Here the UVA and UVB defined according the environmental protection agency, where UVA is having a wavelength: 315-399 nm, and not absorbed by the ozone layer. While, UVB is having a wavelength: 280-314 nm, mostly absorbed by the ozone layer, but some does reach the Earth’s surface.

![Graph showing the effect of TiO\textsubscript{2} dose on KHP degradation](image-url)
Fig. 1-a. COD degradation as a function of time for four different doses of TiO$_2$ at pH 7, UVA & B intensity (12-15 mW/cm$^2$).

![Graph showing COD degradation vs time for different TiO$_2$ doses.](image)

Fig. 1-b. KHP removal efficiencies at different TiO$_2$ doses.

From Figs. 1-a and 1-b, it is clear that 1g/l of TiO$_2$ was the optimum dose with a removal efficiency of about 63%. At lower doses (0.25 and 0.5 mg/l) the removal efficiencies are less than that obtained for 1g/l (36% and 47% respectively) due to insufficient surface area and as a result in free radical generation. On the other hand, at the dose of 2g/l, the turbidity of the solution impedes penetration of UV light, and again limited the free radicals formation, which is clearly shown in fig. 1-b, as it has the lowest removal efficiency (15%). These findings are function of the geometry and working conditions of the photoreactor. These figures also show the zero catalyst dose experiments which carried out to confirm that KHP does not degrade in the absence of TiO$_2$.

2. Effect of KHP initial concentration

Figures 2-a and 2-b, show the effect of initial KHP on COD and removal efficiency. It is found that KHP degradation and removal percentage is highly concentration dependent parameter; increasing the initial concentration of KHP results in reduction of percentage...
removal. This could be justified as the increase of KHP that adsorbed on the surface of TiO₂ will absorb light and photons, hence this will reduce the formation of hydroxyl radicals, and this will decrease the relative number of hydroxyl radicals attacking the compound (Daneshvar et al., 2005, Ong et al., 2009).

Fig. 2–a. COD degradation as a function of time for different initial KHP concentrations at 1g/l TiO₂, pH 7 and UVA & B intensity (11-15mW/cm²)
Fig. 2-b. Removal efficiencies at different initial concentrations of KHP.

3. Effect of initial pH

The pH of the aqueous solution is significantly affecting TiO$_2$ capacity including the size of the aggregates that forms and the particle’s charge. The pH at which the surface of an oxide is uncharged is defined as the Zero Point Charge (pHzpc), for TiO$_2$ it is around pH 7 (Singh, and Thakur, 2011).

Upon hydration, surface hydroxyl groups (TiOH) formed on TiO$_2$. According to equations (1) and (2) these surface hydroxyl groups can undergo reactions of proton association or dissociation, thereby bringing about surface charge which depends on pH as follow:

\[
\text{TiOH} + \text{H}^+ \leftrightarrow \text{TiOH}_2^+ \quad (1)
\]

\[
\text{TiOH} \leftrightarrow \text{TiO}^- + \text{H}^+ \quad (2)
\]

Where TiOH$_2^+$, TiOH, and TiO$^-$ are positive, neutral and negative surface hydroxyl groups respectively. Hence, TiO$_2$ surface will remain positively charged when pH < 7, and negatively charged when pH >7 (Ong et al, 2009). A low pH is associated with a positively
charged surface which cannot provide hydroxyl groups that needed for hydroxyl radical formation, consequently, the rate of KHP degradation may decrease. On the other hand, higher pH values can provide higher concentration of hydroxyl ions (OH\(^-\)) to react with the holes to form hydroxyl radicals (OH\(\cdot\)), thereby enhancing the photo-degradation of

KHP is present at pH 7 as hydrogen phthalate, that is it could be adsorbed onto the catalyst surface. At higher pH values (>7) the KHP is in di-ionic negative form (Eq. 2) which would lead to repulsion by the catalyst surface, resulting in negligible adsorption of KHP (Alhakimi \textit{et al} 2003).

Refering to Figs. (3-a and 3-b), COD removal efficency increases as pH increases, which means that although KHP has not adsorbed on TiO\(_2\) surface, but it degrades more efficiently with the increasing of pH. This suggests that the hydroxyl radicals attack is responsible for the degradation of KHP under these conditions, and it is not removed by adsorption. Further more, at alkaline conditions, the hydroxyl anions act as receptors of the photogenerated holes, hence hydroxyl radicals are easily generated near the TiO\(_2\) surface, which resulted in efficient degradation as pH increases. Form fig. 3-a, there is no clear difference in efficiency removal between pH 7 and pH 8 (76% and 78% respectively), but at pH 9, the removal efficiency is much higher (94%), indicating more generation of hydroxyl radical.
Fig. 3-a. COD degradation as a function of time at different initial pH of KHP solution, at 1g/l TiO$_2$ and UVA & B intensity of (10-15 mW/cm$^2$).

Fig. 3-b. Removal efficiency at different KHP initial pH solutions.
4. Reaction kinetic Study

To find out the reaction order, for the degradation of KHP two assumptions for reaction order will be proposed, a first order and zero order. The experimental data is fitted for both first and zero order reaction, by plotting \( \ln(C_0/C) \) versus time, and \( (C_0 - C) \) versus time respectively and is shown in figures 4 and 5. Where \( C_0 \), and \( C \) are the initial concentration of KHP and concentration of KHP at any time respectively (mg/l). Figure 4 shows the fitting for a first order reaction rate. As is shown from figure 4, and 5 at lower KHP concentration the order of the reaction is best fitted with zero order and high KHP concentration is best fitted with first order reaction order. This basically means that this reaction is of a shifting order, that is, zero order at low concentrations with reaction rate constant of 23.53 mg L\(^{-1}\)h\(^{-1}\), and first order at high concentrations with rate constant of 0.6225 h\(^{-1}\) (fig. (6)). This means that when the concentration is relatively low (50ppm) the surface of the catalyst is saturated (fully covered) with the KHP molecules and the reaction is independent of the concentration, and as the reaction proceeds (degradation of KHP) more area will be available, thus the process is concentration dependent, and hydroxyl radical generation increases (Figure 6).
Fig. 4. Linear variation of \( \ln(C_0/C) \) versus time for the photocatalytic degradation of KHP at different initial concentrations.
Fig. 5: Linear variation of \((C_0 - C)\) versus time for the photocatalytic degradation of KHP at different initial concentrations.

\[
\text{Fig. 6. Shifting order of the photocatalytic reaction at 50 (mg/l) KHP.}
\]

5. Secondary Treated Wastewater in Batch Reactor

Secondary treated wastewater effluents of a decentralized treatment plant located near by the university set for tertiary treatment by using using titanium oxide for photocatalytic detoxification. Table 2 shows annual average of analyses for major parameters in treated wastewater samples. Table 2, shows the average annual analysis results of treated wastewater
obtained from this selected septic tank. This table can also reveal that the COD value is twice that of BOD, and a high concentration of bicarbonate, chloride, nitrate and sulphate. These parameters have a considerable effect on the photooxidation process as will be discussed later.

Table 2. Average annual analyses for the secondary treated wastewater from a selected local septic tank

<table>
<thead>
<tr>
<th>parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.74</td>
</tr>
<tr>
<td>EC (µs/cm)</td>
<td>1831.6</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>66.7</td>
</tr>
<tr>
<td>Ca$$^{++}$$ (mg/l)</td>
<td>72.9</td>
</tr>
<tr>
<td>Mg$$^{++}$$ (mg/l)</td>
<td>32.5</td>
</tr>
<tr>
<td>TH (mg/l) (Total hardness)</td>
<td>300</td>
</tr>
<tr>
<td>HCO$$\text{$_3$}$$ (mg/l)</td>
<td>341</td>
</tr>
<tr>
<td>Cl$$^-$$ (mg/l)</td>
<td>240</td>
</tr>
<tr>
<td>Na$$^+$$ (mg/l)</td>
<td>251</td>
</tr>
<tr>
<td>K$$^+$$ (mg/l)</td>
<td>28.6</td>
</tr>
<tr>
<td>PO$$\text{$_4$}$$ (mg/l)</td>
<td>16.6</td>
</tr>
<tr>
<td>NO$$\text{$_3$}$$ (mg/l)</td>
<td>29.6</td>
</tr>
<tr>
<td>SO$$\text{$_4$}$$ (mg/l)</td>
<td>116</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>102</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>218</td>
</tr>
<tr>
<td>TSS (mg/l)</td>
<td>44</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>1118</td>
</tr>
</tbody>
</table>

5.1. Effect of Organic and Inorganic Components on Removal Efficiency
Three doses of titanium oxide photocatalyst examined in this experimental work namely (0.25, 0.5 and 1 g/l TiO$_2$) in addition to a secondary treated wastewater sample without catalyst to ensure that no oxidation occurs naturally. From Fig. 7, it is found that 1g/l removes about 45% of the initial COD, while lower removal efficiencies are found for 0.25g/l and 0.5g/l, although the turbidity at 1g/l is six times that at 0.25g/l and three times of 0.5g/l. That is the surface area available for photocatalysis enhances the photooxidation process. But this will reduce the removal efficiencies when compare it with that for KHP solution, and can be attributed to the presence of organic and inorganic compounds in wastewater which has its significant effect on the oxidation process in different manners.

![Fig. 7. COD degradation as a function of time at different TiO$_2$ doses for secondary treated wastewater at fixed pH 8 and UVA&B intensity (7-11) mW/cm$^2$.](image)

The effectiveness of degradation process is not only demonstrated by decomposition of original compounds, but also by completely disappearance. Although eliminating the toxicity of parent compounds is desirable, but the main objective is to mineralize all pollutants including the intermediate by-products, which may be, in some cases, more toxic and persistent than the parent compounds. However, it is very difficult to identify all the intermediary compounds en-route to
complete mineralization (Czech, and Rubinowska (2013), Gilmour, (2012), Galvez, and Rodriguez (2003)). Therefore, COD as a colligative property indicates the degree of mineralization for all organic compounds in the sample.

Inorganics that are naturally occurs in wastewater inhibit the photocatalytic oxidation by generating radicals that are less reactive than hydroxyl radicals. The presence of carbonate and bicarbonate has always disadvantageous effects on the oxidation of organic pollutants by the photocatalysis. Dissolved carbonate species act as hydroxyl radical scavengers in water. The resulting carbonate radical is a weaker oxidizing agent that hardly reacts with other organic molecules. Furthermore, bicarbonate anions have the strongest inhibition on the photocatalytic process because they are effective hydroxyl radical scavengers (Sugihara (2010)). This can be attributed to the ability of bicarbonate ions, to react with hydroxyl radicals yielding carbonate radicals. However, photocatalytic degradation of wastewater does not completely inhibit by bicarbonate (Zhang, W. (2005)).

On the other hand, the photocatalytic oxidation process is significantly affected by pH of the aqueous solution, because the species of the reaction compounds and its adsorption equilibrium on the TiO₂ depends on the pH values of the reaction solution. In this experiment work, pH was in the range of 7-8, thereby bicarbonate was abundant, and adsorption was not expected, as the surface charge of TiO₂ is negative so repulsion eliminated adsorption of bicarbonate ions, but their effect as hydroxyl radical scavengers still exists.

The nutrients compounds containing nitrogen, phosphorous and potassium were not decomposed under solar light, because these components existed in their most oxidized forms, NO₃⁻, PO₄³⁻, and K⁺ in the nutrient solution. Therefore, this system could be considered as a nutrient –saving technology (Hashimoto, and Fujishima (2005)). On the other hand it is well known phenomena that the hydroxyl radicals formed by interaction of NO₃⁻ with UV light play an important role in the degradation of micro-pollutants in water. That is the presence of nitrate acts as an inner filter substance to reduce the UV adsorption by TiO₂, resulting in lower photocatalytic activity of TiO₂ (Zhang, W. (2005)).

Lower concentrations of SO₄²⁻ would inhibit the photocatalytic oxidation significantly, since SO₄²⁻ reacts with both h⁺ and hydroxyl radicals forming SO₄• which is less reactive than
OH\textsuperscript{•}, therefore, the photocatalytic oxidation rate will decrease as SO_4^{2-} concentration increased (Zhang, W. (2005)).

Chloride ions present in wastewater in relatively high concentrations, the competition between organic matter and Cl\textsuperscript{−} ions for surface active sites of TiO\textsubscript{2} would be noticeable for the higher concentration of Cl\textsuperscript{−} ions, leading to lower efficiency in photocatalytic reactions (Zhang, W. (2005)).

In general, these components reduce the overall removal of organic matter measured as COD to: 25% for 0.25g/l, 34% for 0.5g/l and 45% for 1g/l.

Another important factor that can be taken into consideration is the solar light intensity. For the degradation of KHP the UVA&B intensity was in the range of (10-15 mW/cm\textsuperscript{2}) as the experiments conducted during June, July and early August. While for treated wastewater samples, the experiments conducted during late August, September and early October, the UVA&B intensity was in the range of (7-11 mW/cm\textsuperscript{2}). This behavior of the intensity eventually affected the photocatalytic process, but it was not avoidable, and several studies examined such conditions under lower values of solar UV intensities.

5.2. Effect of Initial pH on the Removal Efficiency

Figures 8-a and 8-b show the affects of pH results on the removal efficiency, as it can be seen the pH has no great influence on photooxidation on treated wastewater sample, which could be attributed to the presence of a matrix of organic and inorganic components that behave in different ways under different pH values.
Fig. 8-a. COD degradation as a function of time at different initial pH for secondary wastewater samples at 1g/l and UVA&B intensity (7-11) mW/cm².
Fig. 8-b. Removal efficiency at different initial pH for secondary treated wastewater samples.

5.3. Photo disinfection of Secondary Treated Wastewater

Wastewater contains a range of pathogens, one of the important goals is the inactivation of pathogens during the treatments to minimize the public health risks associated with reclaimed water (Costan-Longares et al, (2008)). Disinfection is an essential treatment that safeguards consumers against pathogenic microorganisms in reclaimed water, and chlorine-based disinfectants are widely utilized disinfectants for drinking water and reclaimed water worldwide (Environmental Protection Agency). (2012). Reclaimed water contains a high level of organic matter, which potentially reacts with the disinfectants but also provides nutrition for microorganisms.

Photocatalytic detoxification includes both removal of toxic material and eliminating the pathogenic effect of wastewater, and for the purpose of disinfection of wastewater samples by photocatalyst under solar UV, E-Coli counts using IDEXX technology carried out for each run.

5.3.1. Effect of Catalyst Load on Photo disinfection
Figure 9 shows the effect of the three different doses of TiO$_2$ on E-Coli survival, in addition to zero catalyst load. It is clear that TiO$_2$ dose of 1g/l exhibits the fastest removal in terms of E-Coli count and time required to reach this count. It is worth to note that zero dose of the catalyst behaves in a better response than 0.25g/l and 0.5g/l doses. The realistic reason for this is that the turbidity of these solutions slows down the rate of photodisinfection, although finally after 8 hours they have nearly the same count. While in 1g/l dose, and in spite of high turbidity (about 3500 NTU), the rate of disinfection was the highest due to direct UVA exposure, which can induce cellular membrane damage. The activity of UVA has been attributed to the generation of reactive oxygen species (ROS). Hydroxyl radical is suggested to be the main species responsible for microorganism inactivation in several photocatalytic disinfection studies; however, some papers do report the involvement of other ROS such as H$_2$O$_2$, O$_2$ (Alrousan, et al, (2009)).

![Fig. 9. E-Coli count as a function of time for different TiO$_2$ doses, at pH and UVA&B intensity (7-11) mW/cm$^2$.](image)
5.3. Effect of pH of Wastewater on Photo disinfection

Potential changes on the bactericidal activity of TiO$_2$ due to slight changes of the pH of the samples were investigated for two pH values (pH 8 which is the pH of the wastewater sample initially, and pH 9. Figure 10 shows that at pH 9 the rate of photodisinfection is higher until 6 hours where both pH’s have nearly the same count, and zero count was attained after 8 hours.

![Fig. 10. E-Coli count as a function of time for different initial pH of wastewater sample at 1g/l TiO$_2$ and UVA&B intensity (7-11mW/cm$^2$).](image)

Although chlorine is a widely utilized disinfectant and is a leading contender for disinfection of reclaimed water, but reactivation and regrowth of bacteria were most likely to occur after exposure to lower chlorine doses, and extents of reactivation decreased gradually with increasing chlorine dose (Li, et al, (2013), Li, (2013)). In this study, test for re-growth of E-Coli were examined for all treatment processes of treated wastewater. It is noted that no regrowth occurred after 24h storage in dark for any of the examined samples, which indicates complete inactivation of E-Coli.
Conclusions

This study has explored photocatalytic oxidation of potassium hydrogen phthalate (KHP) and organic matter present in secondary treated wastewater measured as COD, in addition to disinfection of that wastewater by inactivation of E-Coli bacteria as indicator bacteria.

From the results, it is evident that TiO$_2$ is efficient in photooxidation and reducing COD values. The kinetic model was first order regarding high KHP concentrations and zero order for low KHP concentrations.

The removal efficiency found to be highly dependent on the catalyst load up to certain concentration (1 g/l TiO$_2$) under the conditions of this study, beyond which the turbidity of the slurry solution prevents the light penetration. pH has a great influence on removal efficiency for KHP, as pH increase the formation of hydroxyl radicals increase, thus the photocatalytic activity enhances and 94% removal efficiency of KHP was obtained.

The photocatalytic efficiency in the real wastewater sample under the optimized conditions were between 44-50% depending on the catalyst load, and on initial pH of the sample, although pH has not clear role in the domain examined in this study pH (7-9). The presence of inorganic ions, (i.e. sulphate, nitrate, and bicarbonates) and organic matter suppressed the photocatalytic activity.

Disinfection of secondary treated wastewater was accomplished by photocatalysis in both reactors within the first 6 hours, with the advantage in terms of non-recovery of inactivated E-Coli after 24 hour incubation in dark thus ensuring public health security during wastewater reuse.

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