Titanium dioxide catalyzed photocatalytic degradation of carboxylic acids from waste water: A Review

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Abstract

Among the new oxidation methods in advanced oxidation processes, heterogeneous photocatalysis based on UV/ titanium dioxide is one of the emerging technologies for degrading and totally mineralizing toxic and highly stable carboxylic acids from waste water has attracted great attention in last decade. The aliphatic and aromatic carboxylic acids are widely used as reactants or produced as main products or byproducts in various chemical process industries. These chemical process industries generates waste water containing significant amount of carboxylic acids, which need to be removed from waste water before disposal to natural water bodies due to the environmental restrictions and their hazardous effects on flora and fauna. This paper reviews photocatalytic degradation (PCD) process for various carboxylic acids in detail, including basic mechanism of titanium dioxide, effect of carboxylic acid structure and various reaction parameters like effect of initial concentration and kinetic study, catalyst loading, pH, adsorption and deactivation of the photocatalyst. A critical analysis of the available literature has been made and some general conclusions have been drawn related to the above mentioned parameters. The photocatalytic degradation pathways for carboxylic acids are also discussed to understand this process thoroughly.

Introduction

Water is one of the most important natural resources essential for sustaining of life on the planet. In the process of rapid industrialization and increase in human population, the demand for pure water is increasing. Huge amount of fresh water is used in different chemical process industries such as petroleum and petrochemical, organic and inorganic, pharmaceutical, dyes and pigments, fertilizer, chlor-alkali, paints, textile, pulp and paper industries. In addition, water is the most widely used solvent in industry. These chemical process industries generate a large amount of waste water containing toxic and complex pollutants. The surface and ground water sources in major industrial area are contaminated with various inorganic and organic components. The pollutant nature and composition varies depending on presence of solvents, volatile organics, chlorinated volatile organics, pesticides, phenolic compounds, other aromatic compounds, aliphatic or aromatic carboxylic acids, different types of dye depending upon the application of water and various raw materials used in chemical process industries. In order to address this significant problem of treatment of waste water, there is growing demand for effective, economic, and environmental friendly waste water treatment technologies, where all pollutants in the waste water are removed effectively.
The major users and producers of carboxylic acids are petrochemical, pharma, paints, dyes and pigments industries. Benzoic acid and its chloro-, nitro- derivatives are mostly found in the waste water of pharma industries. Benzoic acid and phthalic acids are found in effluents generated by purified terephthalic acid (PTA) plants [1-2]. For each ton of PTA manufactured, approximately 3-4 m³ of waste water generated. Phthalic acid is also present in the waste water of dyes and paint industries, where it is used in acylation, esterification, etc. The effluents generated by these industries contains significant amount of carboxylic acids.

In recent years, the TiO₂ catalyzed photocatalytic degradation (PCD) in the presence of UV and oxygen has attracted attention of researchers for remediation of hazardous pollutants in water. The advantages of PCD over conventional treatment techniques are degradation of a broad range of organic pollutants, lower cost, and mild operating conditions [3]. The TiO₂ catalyzed PCD of various groups of organic pollutants like alcohols, phenols, carbonyls and carboxylic compounds, aromatics, halocarbons etc. has been reported extensively [3-8].

The removal of several aliphatic carboxylic acids [9-11] as well as aromatic acids such as benzoic acid, polycarboxylic acids, salicylic acid, chlorobenzoic acids, etc. [12-17] from water using TiO₂ catalyzed PCD has been reported. Besides this, photocatalytic degradation of the higher aliphatic carboxylic acids such as branched C₄ and C₅ aliphatic acids using titanium dioxide has also been studied [18].

The present review focuses on TiO₂ catalyzed PCD of carboxylic acid i.e., aliphatic and aromatic carboxylic acid and studying the influence of various parameters affecting PCD of carboxylic acids, i.e., molecular structure on the kinetics and mechanistic pathway, effect of initial concentration, pH, adsorption and deactivation of catalyst.

**Photocatalytic degradation using TiO₂**

Heterogeneous photocatalysis can be carried out in aqueous solutions, gas phase or pure organic liquid phases. The overall process of heterogeneous photocatalysis can be explained by five basic steps.

(i) Transfer of the reactants in the fluid phase to the surface of photocatalyst
(ii) Adsorption of at least one or more reactants on the surface
(iii) Reaction in the adsorbed phase
(iv) Desorption of the product/products
(v) Removal of the products from the interphase

The photocatalytic reaction occurs in the adsorbed phase. The only difference between the conventional catalysis and photocatalysis is the mode of activation energy. In the photocatalysis, thermal activation energy is replaced by the photonic activation. Hoffmann et al. proposed the heterogeneous photocatalytic reactions into various mechanistic steps [5]. A photo-excited TiO₂ generates an electron (e⁻) and hole (h⁺) when photons of energy equal to or greater than the band gap of the semiconductor (3.2 eV for anatase phase titanium dioxide) are incidents upon its surface as shown in Fig. 1.
TiO\textsubscript{2} \rightarrow e^- + h^+ \tag{1}

Electron transfer from the adsorbed substrate (RX\textsubscript{ad}), adsorbed water or the OH\textsubscript{ad} ion, to the electron-hole.

\[ h^+ + RX\textsubscript{ad} \rightarrow RX^{+}\textsubscript{ad} \tag{2} \]

\textbf{Fig. 1,} Schematic presentation of the electron-hole generation in a photocatalyst particle and some of the mechanisms involved

\[ h^+ + H_2O\textsubscript{ad} \rightarrow \cdot OH\textsubscript{ad} + H^+ \tag{3} \]

\[ h^+ + OH\textsubscript{ad} \rightarrow \cdot OH\textsubscript{ad} \tag{4} \]

The third step is due to high concentration of OH\textsuperscript{-}, water dissociates into ions.

\[ H_2O \rightarrow OH^-\textsubscript{ad} + H^+ \tag{5} \]

Molecular oxygen acts as an acceptor species in the electron-transfer reaction.

\[ e^- + O_2 \rightarrow O_2^- \tag{6} \]

Super oxide anions (O_2\textsuperscript{-}) can be involved in the following reactions.

\[ O_2^- + H^+ \rightarrow HO_2^\cdot \tag{7} \]

\[ H^+ + O_2^- + HO_2^\cdot \rightarrow H_2O_2 + O_2 \tag{8} \]

Photoconversion of hydrogen peroxide gives more \cdot OH free radical groups.

\[ H_2O_2 + hv \rightarrow 2 \cdot OH \tag{9} \]
Finally, $\cdot$OH radicals oxidize organic adsorbed molecules ($R\ X_{ad}$) onto the surface of the titanium dioxide particles.

\[
\cdot OH_{ad} + R\ X_{ad} \rightarrow \text{Intermediates} \rightarrow CO_2 + H_2O \quad (10)
\]

The $\cdot$OH radicals are very active oxidizing agent and attack the pollutant molecule to degrade it into mineral acids including carbon dioxide and water.

### Degradation of carboxylic acids and its mechanism

TiO$_2$ catalyzed PCD of carboxylic acids are usually initiated via two routes. The first route is Photo Kolbe’s decarboxylation of carboxylic acid followed by reaction of $\cdot$OH radical (hydroxylation), whereas the second route involves hydroxylation followed by Kolbe’s decarboxylation (Fig. 2). The nature of substituents presents in carboxylic acid and reaction conditions decides the mechanism of PCD. The mechanistic pathways of PCD of some carboxylic acids are discussed here.

![Generalized mechanistic pathways for PCD of carboxylic acids](image-url)

**Fig. 2, Generalized mechanistic pathways for PCD of carboxylic acids**

Wolff et al. [19] have examined the photocatalytic oxidation of acetic acid on TiO$_2$. It has been proposed that hydroxyl radicals ($\cdot$OH) attack acetate ions mainly, at the methyl group.

\[
CH_3COOH + \cdot OH \rightarrow \cdot CH_2COOH + H_2O \quad (11)
\]

In the presence of oxygen, the radicals thus formed react quickly with molecular oxygen leading to the formation of CHOOCOOH, HOCH$_2$COOH, HOOCH$_2$OOCH$_2$COOH, HCHO, and CO$_2$. Direct electrochemical oxidation of acetate results in the well-known Kolbe decarboxylation with the formation of a methyl radical.

\[
h^+ + CH_3COO^- \rightarrow \cdot CH_3 + CO_2 \quad (12)
\]
In this case, the intermediate formation should include \( \text{CH}_3\text{COOH}, \text{CH}_3\text{COOCH}_3, \text{HCHO}, \text{CH}_3\text{OH}, \text{HCOOH} \) and \( \text{H}_2\text{O}_2 \). Wolff et al. [19] reported that at pH 10.6, the main products of the photocatalytic oxidation of acetate on \( \text{TiO}_2 \) were glycolate and formate with trace amount of glyoxylate. On the other hand, under acidic conditions they found only formate and formaldehyde. The formation of glycolate and glyoxylate is taken as evidence for the oxidation of acetate via hydroxyl radicals.

Hermann et al. [20] found that malic acid could completely be mineralized by photocatalytic degradation and proposed four parallel decomposition pathways. One of the proposed routes for degradation of malic acid is by decarboxylation in the \( \alpha \)-position from the \( \text{OH} \) group according to photo-kolbe reaction via formation of 3-oxopropanoic acid (\( \text{HCO-CH}_2\text{COOH} \)), malonic acid, acetic acid, formic acid and finally carbon dioxide. The other carboxylic group can also be linked to the surface, since 2-hydroxypropanoic acid (lactic acid) is also formed via the photo-Kolbe process. Competitive oxidation via \( \text{HO} \) radicals also occur, since fumaric/ maleic (H abstraction) and tartaric (\( \text{OH} \) addition) acids are present as intermediates. In the case of photocatalytic degradation of Oxalic acid [21-22], the formation of unstable intermediates such as \( \text{HCO}_3 \) [21] and \( \text{CO} \) are observed [23]. The PCD of formic acid oxidizes to \( \text{CO}_2 \) in a single step without forming long lived intermediates [24].

Sakata et al. [25] found alcohols, acids, aldehydes (or ketones), and alkanes as intermediates during the photocatalytic degradation of \( \text{C}_2-\text{C}_4 \) and 4-oxopentanoic acids in deareated solutions. The participation of either holes and \( \text{H}_2\text{O} \) or holes and \( \text{HO} \) is proposed [25]. In PCD of octanoic acid, heptanol and heptanoic acid are identified as intermediates [26]. Both hole and \( \text{HO} \) participation is proposed to produce an alkyl radical, which can further react with oxygen. Guillard [10] reported the PCD of butanoic acid in aqueous \( \text{TiO}_2 \) dispersions by two steps. First, an alkyl radical is formed; either by \( \text{HO} \) attack or by a hole and then, this alkyl radical reacts with oxygen, organic molecule or photocatalyst surface species.

Serpone et al. [27] studied the photocatalyzed degradation and mineralization of the linear carboxylic acid \( \text{C}_1-\text{C}_5 \) series, namely, formic acid, acetic acid, propanoic acid, butanoic acid, and valeric acid. The PCD of linear carboxylic acids depends on their chain length in case of \( \text{C}_2-\text{C}_5 \) series and formic acid degrades faster into carbon dioxide and water than other acids with no intermediates formed.

Herrmann et al. [16] reported the photocatalytic degradation of three isomers of chlorobenzoic acids (CBA) in the aqueous medium in relation with the nature and the position of both substituents on the aromatic ring. The three pollutants disappeared from water in the following order: 3-CBA < 2-CBA < 4-CBA, the para position being the most reactive. The initial step of CBA disappearance was the decarboxylation of the molecule (photo-Kolbe reaction) with an initial rate of \( \text{CO}_2 \) formation equal to that of the disappearance of CBA. All the intermediate products found correspond to the successive hydroxylations of the corresponding chlorophenol obtained after the initial photo-Kolbe reaction. In the case of 2- CBA, primary intermediates correspond to successive hydroxylations of the aromatic ring, either at C-H or at C-Cl bond levels. They are mainly 2-chlorophenol, 4-chlororesorcinol, chlorohydroquinone and catechol. For 3-CBA, the first intermediate identified was 3-chlorophenol which corresponds to a decarboxylation and a subsequent hydroxylation at the same site of the molecule. 3-chlorophenol completely mineralizes via forming 4-chlorocatechol and chlorohydroquinone as intermediates. 4-CBA degradation produced mainly 4-chlorophenol resulting from an initial decarboxylation of 4- CBA, 4-chlorocatechol and 4-chlororesorcinol. All the intermediates formed during PCD of CBA were detected by HPLC and/or by GC/MS.
Hermann et al. [17] also studied the photocatalytic degradation of three polycarboxylic (hemimellitic (Hem), trimellitic (Tri) and pyromellitic (Pyro)) acids. The three molecule disappearance rates followed the order Pyro > Hem > Tri. The higher rate of disappearance of Pyro may be related to the higher number of carboxylic groups, which readily decompose as CO₂ according to the photo-Kolbe reaction. The two competitive initial steps of attack of the molecules corresponded (i) to a hydroxylation reaction induced by photogenerated •OH radicals and (ii) by a decarboxylation (photo-Kolbe) reaction resulting from the direct attack of one carboxylic group by a positive photo-hole. The loss of several carboxyl groups leading to benzoic acid formation was observed before the aromatic ring opening. Several aliphatic acidic fragments were detected, such as malonic and succinic acids using either by HPLC and/or by GC/MS. Interestingly, a condensation product was detected, which indicated that some carboxylic radicals could attack a Tri molecule and form a Pyro molecule. Finally, all these acid intermediates could be photo decomposed into CO₂.

Ajmera et al. [12] found salicylic acid, p-hydroxybenzoic acid, 2,3-dihydroxybenzoic acid, and 2,5-di- hydroxybenzoic acid as intermediates during the PCD of benzoic acid under different conditions. As can be seen from the intermediates, the •OH attack takes place on the ortho and para positions to produce hydroxybenzoic acids and only the dihydroxy derivatives were observed indicating that after the formation of dihydroxy derivatives the ring breaks with further attack of hydroxyl radicals. The -OH group did not replace the -COOH as clearly indicated by the fact that phenol was not detected as an intermediate.

Gandhi et al. [28] studied the photocatalytic degradation of aromatic carboxylic acids such as benzoic acid, o-nitrobenzoic acid, o-chlorobenzoic acid and phthalic acid. The reactivity and degradation pathway of these carboxylic acids were observed to be greatly influenced by the substituent group present in the aromatic ring. The order of degradation of aromatic carboxylic acids was found to be benzoic acid< o-chlorobenzoic acid< o-nitrobenzoic acid< phthalic acid. The aromatic carboxylic acids having an electron withdrawing groups such as –COOH, –NO₂ and –Cl were comparatively more reactive for PCD than unsubstituted aromatic acid i.e., benzoic acid. The degradation of ortho substituted benzoic acids having electron withdrawing groups like -COOH, –NO₂ and –Cl follows different mechanistic pathway than that of benzoic acid. In photocatalytic degradation of phthalic acid, the salicylic acid was identified as main intermediate using HPLC. The formation of salicylic acid indicates that phthalic acid first undergoes Kolbe’s decarboxylation resulting into a free radical, which reacts with •OH radical. Salicylic acid may react with •OH radicals to form 2,3-dihydroxy and 2,5-dihydroxy benzoic acids, which are reported to be reactive intermediate for ring opening reactions and finally oxidized to carbon dioxide and water [19]. In photocatalytic degradation of o-nitrobenzoic acid and o-chlorobenzoic acid, o-nitro and o-chloro phenols formation was observed respectively, which indicates that these intermediate products were also formed by Kolbe’s decarboxylation followed by reaction of •OH radicals. The PCD mechanism of benzoic acid was found to be different from that of ortho substituted benzoic acids (phthalic acid, o-nitrobenzoic acid and o-chlorobenzoic acid). The benzoic acid being less adsorbed over titanium dioxide undergoes reaction with •OH radicals in the solution followed by decarboxylation. The benzoic acid reacts with •OH radical to form salicylic acid as intermediate, which undergoes photodegradation as discussed for the case of phthalic acid.
Effect of Initial Concentration and Kinetic study of carboxylic acids

Initial concentration of the carboxylic acid is one of the important parameter in waste water treatment. The observed rate constant decreases with an increase in initial concentration of carboxylic acids because of the following reasons [12, 28-29].

(i) The main steps of PCD process occur on the surface of solid catalyst. So, a high adsorption capacity is associated with reaction and at a high initial concentration all the active sites of photocatalyst are occupied. A further increase in concentration does not affect the actual catalyst surface concentration, and therefore, this may result in a decrease of the observed first order rate constant [12, 28-29].

(ii) Intermediates generated during PCD process (as discussed in section 3) also affect the rate constant of their original compounds. A higher initial concentration will result in a higher concentration of adsorbed intermediates, which may affect the overall rate of the reaction.

(iii) As the initial concentration of carboxylic acid increases the path length of photons entering the solution decreases, which results in lower photon adsorption on catalyst particles and result in lower photocatalytic reaction rates [14].

The photocatalytic degradation of various carboxylic acids using titanium dioxide can be generally given by the Langmuir–Hinshelwood kinetics model [12, 30-31]

\[
\frac{dC}{dt} = \frac{(k \cdot K \cdot C)}{(1 + k \cdot K \cdot C)}
\]

(13)

where \((\frac{dC}{dt})\) is the rate of degradation, \(k\) the apparent reaction rate constant , \(K\) the adsorption coefficient of the substance to degraded and \(C\) concentration of carboxylic acid. In case the concentration of the substances to be degraded exceed the saturation coverage of the TiO\(_2\) surface, i.e. \(K \cdot C >> 1\), equation (13) simplifies to a zero-order rate equation.

\[
\frac{dC}{dt} = k
\]

(14)

Some of the carboxylic acids like formic acid, phenoxyacetic acid, 2-chlorobenzoic acid, 3-chlorobenzoic acid and 4- chlorobenzoic acid [16], p-hydroxybenzoic acid [32] follow zeroth kinetic order interpreted by a Langmuir-Hinshelwood mechanism involving a saturation of the adsorption sites. For very low concentration (i.e., \(K \cdot C << 1\)), the Langmuir-Hinshelwood equation (13) simplifies to a pseudo-first order kinetic law, where \(k\) is being the pseudo-first order rate constant.

\[
- \ln \left( \frac{C_t}{C_0} \right) = k t
\]

(15)

where \(C_0\) is the initial concentration of carboxylic acid at time \(t = 0\) and \(C_t\) is the concentration of carboxylic acid at reaction time \(t\). The semi-logarithmic plot of \([-\ln \left( \frac{C_t}{C_0} \right)\] versus time gives straight line and slope of the straight line gives the value of reaction rate constant, \(k\) (time\(^{-1}\)). Some of the carboxylic acids like butanoic acid [10], phthalic acid [28], terephthalic acid [33] and oxalic acid [34] are followed pseudo-first order reaction under given experimental conditions.
Effect of pH

The industrial effluents containing carboxylic acids may be acidic in nature and therefore the pH effect needs to be considered. The reaction pH may influence the surface charge on the photocatalyst, amount of produced OH, net charge of pollutants and also the state of ionization of the substrate, and hence its adsorption.

Subramaniam et al. [32] studied the effect of pH on degradation of p-hydroxybenzoic acid (PHBA). They found that adsorption and degradation attained a maximum close to the zero point charge of degussa P-25 TiO$_2$, at pH 7 and then decreased again as the pH was further increased. They also found that the adsorption and PCD rates having a direct relationship and as adsorption increased the PCD rate of PHBA also increased. In the case of butanoic acid [10] photodegradation, the intermediates formed are pH dependent. At neutral pH, amounts of formic acid and butanoic acid formed are increased, as well as 2-oxobutanoic and oxalic acids are formed, which are not observed at acidic pH (3.6). pH modification can induce changes in the adsorption mode of pollutant molecules. In their study on photocatalytic degradation of dichloroacetic acid (DCA), Bahnemann et al. [35] were detected two different types of adsorbed DCA anions on the TiO$_2$ surface: mono and bi-dentate complexes. In acidic solutions, at pH < 4, bidentate complexes (where both oxygen atoms of the DCA carboxylic group are coordinated to the surface) are in significant amount in the system, while monodentate complexes (attached via one oxygen atom) form the majority at pH > 5.

Ajmera et al.[12] found decrease in PCD rate for benzoic acid as pH is increase from acidic (pH =3.5) to alkaline region(pH= 9) because of the rate of adsorption of the benzoic acid decreased as pH is increased. In the PCD of phenoxy acetic acid [29], p-hydroxybenzoic acid [32], 4-chloro-2-methylphenoxyacetic acid [36] and dichloroacetic acid [37] on TiO$_2$, a similar dependence on pH values was found. However the rate of PCD of benzoic acid [12] is observed to be increased at a very high pH (pH = 11.0) because of the fact that under alkaline pH the concentration of OH$^-$ ions as precursors of OH is relatively high [38].

Effect of Catalyst loading

Generally, the photocatalytic reaction rate of carboxylic acid and efficiency increases with increase in catalyst dosage. This is due to a higher surface area (or number of active sites) of the TiO$_2$ photocatalyst available for adsorption and degradation as the catalyst loading is increased. However, above optimal dosage of catalyst, the rate of PCD of substrate becomes constant or changes marginally [14,17, 28 29]. The reasons for this constant/decrease in PCD rate are (i) the solution opacity increases causing a reduction of light penetration in the solution and a consequent decrease in rate [17, 39-41] and (ii) aggregation of TiO$_2$ particles at high concentrations causing a decrease in the number of active sites. Additionally, at high-TiO$_2$ concentrations, terminal reactions could also contribute to the reduction in PCD rate. The hydroperoxyl (HO$_2^*$) radical formed is less reactive than the hydroxyl radical.

\[
O_2^- + H^+ \rightarrow HO_2^* \quad (16)
\]

\[
H_2O_2 + \cdot OH \rightarrow H_2O + HO_2^- \quad (17)
\]

The optimum value of catalyst loading will strongly depends on the type and initial concentration of the pollutant and the operating conditions of the photocatalytic reactor. So the optimum catalyst loading is different by varying the photocatalytic set-up, types of carboxylic acid and its
concentration. In slurry type of photocatalytic reactor, the optimal catalyst loading for various carboxylic acids reported in the range of 0.15 to 6 g/L for different photocatalysed system and conditions. For example, the optimum catalyst loading is reported to be 2.5 g/l for terephthalic acid [33], 2.5 g/l for phthalic acid [28], 0.6 g/l for benzoic acid [14] and 0.4 % wt/vol for p-hydroxy benzoic acid [32] under given set of operational conditions.

**Light Intensity**

Light irradiation plays a major role in all the photocatalytic reactions because number of generated electron hole pairs generated depends on it. Increase in the incident photons rate would results in an increase in PCD rate of carboxylic acids. The high photon flux increases the probability of collision between photons and activated sites of photocatalyst surface and enhances the rate of PCD. For heterogeneous photocatalysis, the dependency of the kinetic constant (k) on the radiation intensity (I) has been reported by following non linear relationship [42],

\[ k \propto (I)^n \]  

where, n ranges from 0.5 to 1. At low intensity, n is equal to 1 whereas at high intensity, n tends to have a value of 0.5 [9, 43]. Table 1 summarizes the value of n in various systems.

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-4 dichlorophenoxy acetic acid</td>
<td>0.5</td>
<td>38</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>0.89</td>
<td>44</td>
</tr>
<tr>
<td>salicylic acid</td>
<td>0.63</td>
<td>45</td>
</tr>
<tr>
<td>phenoxyacetic acid</td>
<td>0.5</td>
<td>46</td>
</tr>
</tbody>
</table>

**Effect of Adsorption**

There are numbers of research article to show that the rate of degradation of the substrate is dependent on the amount adsorbed on the surface of the photocatalyst [5, 30, 40, 47-49]. Serpone et al. [27] studied The PCD of formic acid was faster than other linear carboxylic acid may be because of higher adsorption on TiO$_2$ surface. Gandhi et al. [28] also found that the higher rate of degradation of phthalic acid attributed to its higher adsorption on photocatalyst surface as compare to o-nitrobenzoic acid, o-chlorobenzoic acid and benzoic acid. In the case of p-hydroxy benzoic acid degradation (PHBA), Subramanian et al. [32] showed that the adsorption and PCD rates having direct relationship and as adsorption increased the PCD rate was also increased. Similar trend is observed for the PCD of formic acid as compare to other linear chain carboxylic acid [27].
Antoine et al. [50] observed pH as critical parameter for the adsorption of PHBA on TiO$_2$ surface. They observed maximum adsorption of PHBA in pH range of 4-5. Dagan and Tomkiewicz [51] showed that adsorption of salicylic acid was indicated by a bright yellow colour on the TiO$_2$ surface. Under UV radiation the yellow color changed to dark brown. This indicates that the adsorption and the reaction are occurring on the surface, followed by decolourization of the surface when the reaction was complete.

Overall, based on the available literature, it is reasonable to conclude that the PCD of the substrate strongly depends on its adsorption on TiO$_2$ surface. The substance which is strongly adsorbed having faster rate of PCD. This also gives clear indication that the reaction must be taking place on the catalyst surface itself.

**Deactivation of photocatalyst**

Deactivation and regeneration of photocatalyst is an important issue for practical applications of titanium dioxide photocatalyst for the removal of carboxylic acid from waste water. The reasons for the deactivation of photocatalyst include (a) the generation of reaction by products /intermediates (as discussed in section 3) which cause the loss of active sites on the surface, and (b) fouling which changes the catalyst surface by blocking pores. The stability and the photoreactivity of the catalyst are strongly influenced by the number of hydroxyl groups. As the reaction proceeds, the density of hydroxyl groups on the catalyst surface decreases, consequently the activity of the catalyst drops. The experimental results indicated that strongly adsorbed intermediates occupied the active sites on the catalyst surface and lead to the loss of photocatalytic activity [16, 52-53].

For real-life application, the PCD must be sustainable. It means that the photocatalysis should be reversible with respective to deactivation caused by oxidized intermediates or absorbed byproducts on the surface of these catalysts. There are several methods used to regenerate deactivated photocatalyst: thermal regeneration [54-55], photocatalytic regeneration [56], and regeneration through washing [57]. However, there is no systematic study available on comparison of various regeneration methods for TiO$_2$ photocatalyst used for degradation of carboxylic acid from aqueous media.

**Conclusions**

Photocatalytic degradation using titanium dioxide is one of the useful methods for treatment of waste water containing various types of carboxylic acid. The mechanism of PCD for carboxylic acids depends on the nature of the substituents present and reaction conditions. The optimum dosage of the photocatalyst is require for PCD of carboxylic acids, depends strongly on the types of carboxylic acid and its concentration. The effect of adsorption also has been analyzed and it has been concluded that the substances which are readily adsorbed are degraded at a faster rate. The initial concentration, light intensity and pH also affect the rate of degradation of carboxylic acids. However, deactivation of photocatalyst is one of the major issue to be addressed to commercialize this process.
References:


Titanium Dioxide Catalyzed Photocatalytic Degradation of Carboxylic Acids from Waste Water: A Review
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