Chapter 5
PHOTOLYTIC/PHOTOCATALYTIC DEGRADATION OF POLYVINYL CHLORIDE PLASTIC WASTES FROM THE ENVIRONMENT

5.1 Introduction

Rigid polyvinyl chloride (PVC) is one of the most widely used thermoplastic materials in the world today with extensive applications due to a variety of beneficial properties such as high chemical resistance, barrier properties and low cost [187-188]. However the disposal of PVC waste in land and water is a major global environmental issue. Most waste plastic products are disposed off by unlawful land filling or burnt thereby leading to serious secondary pollution problems [189-192]. The waste plastics left in the open are exposed to sunlight and other natural conditions of rain, wind, dust etc. Chemical inertness and non-biodegradable nature of PVC make its natural degradation extremely slow. Hence it does not get easily decomposed in natural environment. When PVC products are disposed off by unscientific and improper means, they break down and release harmful chemicals like dioxins.
PVC is a thermoplastic consisting of long chains of monomer vinyl chloride.

\[ n \text{CH}_2=\text{CHCl} \rightarrow [\text{CH}_2-\text{CHCl}]_n^- \]

where \( n \) is the number of monomer units.

Plasticized PVC is obtained by adding plasticizers to rigid PVC.

Heterogeneous photocatalysis is an advanced oxidation process (AOP), widely investigated for the degradation of organic pollutants in water and air [112,154,159,193-194]. Solid-phase photocatalytic degradation of polymers under ambient conditions represents an attractive and efficient technique for the treatment of waste plastics with UV light or sunlight as the irradiation source [195-199]. The basic mechanism of photocatalysis involving hydroxyl radicals has been well established [159].

Semiconductor oxides such as TiO\(_2\) and ZnO and their modifications obtained by doping, immobilizing, metal deposition etc are the most widely used photocatalysts [156-158]. Most of the studies on the photo degradation of plastics are made using TiO\(_2\) as the catalyst, mainly due to its wide availability, stability, non-toxicity and reactivity. Another semiconductor oxide ZnO has received relatively less attention due to its corrosive nature under extreme pH conditions. At the same time ZnO is reported to be more efficient than TiO\(_2\) for the visible light induced photocatalytic degradation of organic pollutants because the former can absorb relatively larger fraction of solar spectrum compared to the latter [158,200]. In photocatalysis photo excitation of the semiconductor oxide promotes valence band electrons to the conduction band thereby generating
electron deficiency or hole in the valence band. Dioxygen provides a sink for conduction band electron forming superoxide anion radical $O_2^-$ which leads to the formation of reactive hydroperoxide radical $HO_2^-$. Holes in the valence band can react with water molecules or hydroxide anion to form OH radicals. The holes can also interact with an adsorbed organic donor leading to its eventual oxidation and possible mineralization.

In this chapter, the possibility of using photocatalysis and photolysis for the safe disposal of PVC plastic is examined. It is an extension of the study reported in previous chapter which showed that photocatalysis can be effectively used for the slow but safe mineralisation of LDPE plastics. The possibility of using TiO$_2$ and ZnO mediated photocatalysis for the degradation of PVC plastic is evaluated and compared. The effects of various reaction parameters on the photocatalytic degradation of PVC is also investigated and optimized.

5.2 Materials and Methods

The sources of various materials used, their characteristics etc are the same as provided in Chapter 4. Ordinary PVC pipes used and discarded after domestic applications were used in the study. The PVC pipe is cut into thin sheets of approximately 25cm length, 1cm breadth and 1mm thickness. Typical samples used are shown in figure 5.1. Various chemicals used in the study were of AnalR grade or equivalent.
As described in Chapter 4, the photodegradation experiments were carried out by placing the strips in a suspension of catalyst/water in a pyrex test tube. The test tubes are placed in lamp-housing box of the photoreactor assembly under eight 8W ultraviolet lamps of wavelength 365 nm. Photodegradation of PVC samples after irradiation was determined based on weight reduction, SEM images, tensile strength and visual observation.

5.3 Results and Discussion

Investigations on the photocatalytic degradation of PVC plastic using ZnO and TiO$_2$ catalysts under identical conditions showed that no significant degradation took place in the absence of UV light or the catalyst suggesting that both catalyst and light are essential to effect its degradation. Preliminary studies presented in figure 5.2 show that TiO$_2$ is more efficient as a photocatalyst compared to ZnO.
The weight loss of PVC plastic does not lead to the presence of organic carbon in water as determined by TOC and COD. This confirms the complete mineralization of PVC into CO₂, water and salts as explained later in this chapter (section-5.3.9).

5.3.1 Effect of dosages of TiO₂ and ZnO

Preliminary investigations of the effect of catalyst dosage on the photocatalytic degradation of PVC plastic were made using both ZnO and TiO₂ catalysts individually under identical conditions. The results are presented in figure 5.3.
Chapter 5

![Graph showing % weight loss vs Concentration (mg/L) for ZnO and TiO2 over Time: 40 hr]

**Figure 5.3**: Effect of dosage of TiO2 and ZnO on the photocatalytic degradation of PVC plastic

The optimum catalyst loading of both ZnO and TiO2 is 1400 mg/L. Above this dosage, the degradation is stabilized or decreases. Possible reasons for the optimum in the catalyst dosage are discussed in Chapter 4, section 4.4.1. Beyond the optimum loading, the light photon absorption coefficient of the catalyst decreases radially. The decrease is steeper in the case of ZnO. However, such attenuation over the radial distance does not obey the Beer-Lambert law due to the strong absorption and scattering of light photons by the catalyst particles [177]. Excess catalyst particles lead to aggregation and screening of light which reduce the effective surface area of the semiconductor oxide being exposed to illumination. This leads to decreased photocatalytic efficiency. The results further showed that TiO2 is significantly more efficient for the photocatalytic degradation of PVC compared to ZnO under identical conditions. Hence all further
investigations in this chapter were carried out using TiO$_2$ as catalyst at the optimized loading as above, unless mentioned otherwise.

5.3.2 Effect of pH

The UV-induced degradation of organics with or without catalyst is reported to be dependent on the pH value of the solution [177]. The effect of pH on photocatalytic degradation of PVC plastic was investigated in the range 2.5-10. The results are presented in figure 5.4.

![Figure 5.4: Effect of pH on the photocatalytic degradation of PVC plastic in presence of TiO$_2$](image)

The pH of the suspension was adjusted before irradiation and was not controlled during irradiation. The degradation is more efficient in the acidic region than in the neutral or alkaline region. Mild degradation of PVC is seen in the acidic region of pH ~2.5 even in the absence of the catalyst or light. However at the natural pH of the catalyst suspension (~ 6.0-7.0), noticeable degradation takes place only in the presence of the
catalyst and light. Degradation at extreme acidic conditions, even if feasible, is not a viable solution economically or ecologically since it requires expensive and hazardous neutralization and disposal processes. Hence it is more prudent to optimize the parameters at the natural pH of the system at which reasonable degradation of the plastic is observed in presence of TiO₂ and light. Hence all further studies are conducted at the natural pH of the reaction system.

5.3.3 Effect of H₂O₂ on the degradation

Hydrogen peroxide is detected as a by-product/intermediate/end product in the photocatalytic degradation of many organic pollutants. Simultaneous decomposition of the H₂O₂ thus formed results in oscillation, i.e., periodic increase and decrease in its concentration [187, 199]. H₂O₂ is detected during the degradation of PVC plastic also in the reaction medium in the present instance. However, since the degradation is very slow, the concentration is very small (< 2 mg/L) and the possible oscillation could not be precisely followed with the analytical techniques available with us. In addition to being an oxidant by itself, the reactive free radicals such as ‘OH and HO₂⁻ formed from H₂O₂ decomposition can enhance the degradation of organics. However, instances of inhibition of the degradation of organics by H₂O₂ also have been reported especially at higher concentrations (of H₂O₂).

The effect of added H₂O₂ at various concentrations on the photocatalytic degradation of PVC plastic is tested under standardized conditions and the results are plotted in figure 5.5. H₂O₂ alone or a combination of TiO₂ and H₂O₂ does not degrade PVC in the dark. The degradation and consequent weight loss occur only under irradiation.
decomposition of PVC, as measured by the weight loss, increases with increase in concentration of H$_2$O$_2$. Optimum H$_2$O$_2$ concentration is 300mg/L. After the optimum, the % degradation decreases sharply.

![Graph showing the effect of H$_2$O$_2$ on the photocatalytic degradation of PVC with and without TiO$_2$.](image)

**Figure 5.5:** Effect of H$_2$O$_2$ on the photocatalytic degradation of PVC with and without TiO$_2$.

The photoactivation of TiO$_2$ and subsequent formation of the reactive ‘OH radicals are shown in reactions (80)-(83). H$_2$O$_2$ is formed primarily as in reaction (84). H$_2$O$_2$ is known to decompose under photocatalytic conditions forming more reactive ‘OH and HO$_2^-$ radicals as in reactions (85) and (86). Further H$_2$O$_2$ itself is a good electron and hole acceptor capable of preventing the recombination of photogenerated electrons and holes on the surface of TiO$_2$.

\[
\text{Semiconductor} + h\nu \rightarrow h^+_V + e^-_C \quad \text{(80)}
\]
\[
h^+_V + e^-_C \rightarrow \text{Heat} \quad \text{(81)}
\]
\[
O_2 + e^-_C \rightarrow O_2^- \quad \text{(82)}
\]
Thus the reactive free radicals ‘OH and HO$^\cdot_2$ formed from H$_2$O$_2$ can enhance the degradation of PVC. However at higher concentration of H$_2$O$_2$ the reactive free radicals as well as the electrons and holes interact more frequently with H$_2$O$_2$ and less with the pollutant.

Thus the concentrations of H$_2$O$_2$ and the more reactive free radical ‘OH become less and this leads to stabilization or even decrease in the degradation of PVC. The concentration effect of H$_2$O$_2$ on the photocatalytic degradation of organic pollutants resulting in transition from enhancement to inhibition was reported by other workers also [185, 188, 201].

5.3.4 Effect of Fenton reagent on the degradation

Since H$_2$O$_2$ at the appropriate concentration, enhances the degradation of PVC, the possibility of combining H$_2$O$_2$ with ferrous salt and the effect of the resultant Fenton reagent on the degradation of PVC is also examined. Efficiency of the Fenton process is very sensitive to reaction
conditions. In particular it depends on the relative concentration of FeSO$_4$ (FS) and H$_2$O$_2$. Hence detailed investigations were made on optimizing the ratio of these critical components for PVC plastic degradation under UV light by varying ratios of FS and H$_2$O$_2$. The results are presented in figure 5.6. The optimization is done both in the presence as well as absence of TiO$_2$. The optimum ratio of FS/H$_2$O$_2$ (mg/L) is identified as 40:200, ie, 1:5 in both cases. Surprisingly TiO$_2$ does not have any additive effect in presence of Fenton reagent. In fact it has slight inhibition effect at lower H$_2$O$_2$ concentration. The effect of Fenton reagent on the degradation of PVC in the dark was investigated in the presence as well as absence of TiO$_2$ and the degradation was found to be almost nil.

\[\text{Figure 5.6: Effect of Fe}^{2+}/\text{H}_2\text{O}_2 \text{ ratio on the efficiency of Fenton degradation of PVC plastic in UV light}\]
Since the Fenton reagent (FR) mediated degradation is almost same with and without TiO$_2$, all further studies with FR were conducted without TiO$_2$. The effect of dosage of Fenton reagent at the optimized ratio (1:5) is tested and the results are shown in figure 5.7. The degradation increases with increase in quantity of FR and reached an optimum at FS:H$_2$O$_2$= 80:400.

![Graph showing the effect of concentration of Fenton reagent on the rate of photodegradation of PVC plastic](image)

**Figure 5.7:** Effect of concentration of Fenton reagent on the rate of photodegradation of PVC plastic

The study of the effect of pH on Fenton reagent shows that the degradation is maximum in the acidic pH and is almost nil in the extreme alkaline conditions. The results are shown in figure 5.8. This is consistent with literature reports according to which Fenton reaction is sensitive to pH [202].
Photolytic/Photocatalytic Degradation of Polyvinyl Chloride Plastic Wastes from the Environment

Investigations on Advanced Oxidation Processes as potential environment friendly techniques for the degradation of plastic pollutants

Figure 5.8: Effect of pH of Fenton reagent on the degradation of PVC plastic

The Fenton degradation of PVC under UV irradiation slows down with time. This slowdown after the initial faster rate may be due to the consumption of $\text{H}_2\text{O}_2$ and corresponding variation in the ratio of components in the Fenton. This is verified by replenishing $\text{H}_2\text{O}_2$, FS and FR itself in the system at two different time intervals, 40 and 80 hr. Addition of $\text{H}_2\text{O}_2$ and addition of FR itself in-between enhances the degradation while the addition of extra FS does not increase the degradation significantly. Hence it may be inferred that FS is not consumed in the system and the initial quantity is sufficient to carry the reaction forward as seen in figure 5.9. The effect is more or less same in the case of in-between added FR and $\text{H}_2\text{O}_2$ indicating that it is the decreasing concentration of $\text{H}_2\text{O}_2$ that is responsible for decrease in degradation with time. Thus under photolysis, the efficiency of the Fenton
reagent mediated degradation can be enhanced and sustained by periodic addition of H$_2$O$_2$.

![Graph showing the effect of in-between addition of FR/H$_2$O$_2$/FS on the Fenton degradation of PVC plastic under UV irradiation.](image)

**Figure 5.9:** Effect of in-between addition of FR/H$_2$O$_2$/FS on the Fenton degradation of PVC plastic under UV irradiation

The basic mechanism of the process may be presented as follows.

The first step in the Fenton reaction is the oxidation of ferrous to ferric ions and decomposition of H$_2$O$_2$ into ‘OH radicals:

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot \text{OH}$$ ..........................................................(91)

The Fe$^{3+}$ is reduced by excess H$_2$O$_2$ to regenerate Fe$^{2+}$ and more free radicals as in reaction (92)

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+$$ .........................................................  (92)
Other possible reactions are:

\[
\begin{align*}
\text{Fe}^{2+} + \cdot \text{OH} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad \text{.......................................(93)} \\
\text{Fe}^{2+} + \text{HO}_2^- & \rightarrow \text{Fe}^{3+} + \text{HO}_2^- \quad \text{....................................... (94)} \\
\text{Fe}^{3+} + \text{HO}_2^- & \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad \text{.......................................(95)} \\
\end{align*}
\]

The highly reactive free radicals can get deactivated by self-scavenging as well as by interaction with other radicals and/or H\textsubscript{2}O\textsubscript{2}.

\[
\begin{align*}
\cdot \text{OH} + \cdot \text{OH} & \rightarrow \text{H}_2\text{O}_2 \quad \text{.......................................(96)} \\
\cdot \text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad \text{....................................... (97)} \\
\text{HO}_2^- + \text{HO}_2^- & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{.......................................(98)} \\
\cdot \text{OH} + \text{HO}_2^- & \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad \text{.......................................(99)} \\
\end{align*}
\]

In the absence of any organic substrate to be oxidized, H\textsubscript{2}O\textsubscript{2} self-decomposes as in reactions (100) and (101).

\[
\begin{align*}
2 \text{H}_2\text{O}_2 & \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \quad \text{.......................................(100)} \\
\text{H}_2\text{O}_2 & \rightarrow 2\cdot \text{OH} \quad \text{.......................................(101)} \\
\end{align*}
\]

In presence of organic molecules (R), such as PVC in the current instance, the degradation can take place as in reactions (102) – (104) or dimerization occurs as in reaction (105). Eventually mineralization takes place as in reaction (106).

\[
\begin{align*}
\cdot \text{OH} + \text{R} & \rightarrow \text{H}_2\text{O} + \text{R}^- \rightarrow \text{(Partial mineralization + Colorless} \\
& \quad \text{intermediates)} \quad \text{....................................... (102)} \\
\text{R}^- + \text{Fe}^{2+} & \rightarrow \text{R}^- + \text{Fe}^{3+} \quad \text{.......................................(103)} \\
\end{align*}
\]
\[ R' + Fe^{3+} \rightarrow R^+ + Fe^{2+} \] ...................................................(104)

\[ R' + R' \rightarrow RR \] ..............................................................(105)

\[ \text{R'} \text{ or R'} \text{ or R}^+ \text{ or RR} + \cdot \text{OH, H}_2\text{O}_2, \text{H}_2\text{O}_2 \text{ etc.} \rightarrow \text{intermediates} \]
\[ \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{salts (mineralization)} \] ..........(106)

5.3.5 Effect of peroxydisulphate on the degradation

Our earlier studies have shown that peroxydisulphate (PDS) can also serve as an accelerator for the degradation of organic pollutants such as petrochemicals, plastics, pesticides and dyes [162]. In view of this, the effect of PDS on the photocatalytic degradation of PVC was investigated in the presence as well as absence of TiO\(_2\). The results with increasing concentration of PDS are plotted in figure 5.10.

**Figure 5.10:** Effect of PDS on the photodegradation of PVC plastic with and without TiO\(_2\)
The degradation of PVC is enhanced by PDS. The effect is concentration dependent with higher concentration favouring increased degradation up to an optimum. The optimum concentration for PDS is 2000mg/L. Above this concentration degradation of PVC is stabilised. As seen from the data in figure 5.10, presence of combination of TiO₂ and PDS gives same degradation of PVC as in the presence of PDS. The comparative effect of TiO₂, PDS and TiO₂+PDS on the photodegradation of PVC, after longer times of UV irradiation is presented in figure 5.11.

**Figure 5.11:** Comparative efficiency of TiO₂, PDS and TiO₂+PDS on the photodegradation of PVC plastic

The results show that TiO₂ alone is much less efficient compared to PDS or TiO₂+PDS. Also PDS and (TiO₂+PDS) maintain comparable efficiency at all reaction times, i.e., the relative efficiency of the oxidants is not affected by duration of irradiation. At the optimum concentration of
PDS, photolysis could achieve over 7% of PVC mineralisation in 400 hr time. During the same period the degradation effected by TiO$_2$ only is $\sim$3.5%. Based on this result, it is seen that PDS alone is comparatively better for the degradation of PVC. The effect of time on the photodegradation of PVC in the presence optimised dosage (2000mg/L) of PDS is tested in detail and the results are plotted in figure 5.12.

\[ \text{Figure 5.12: Effect of PDS on the degradation of PVC plastic} \]

The degradation increases with time but the rate slows down towards the later stages as in the case of most photolytic degradation reactions.

Comparison of degradation in presence of other oxidants shows that PDS is a much better oxidant compared to H$_2$O$_2$ and Fenton reagent. At the optimized concentrations of the respective oxidants, PDS is at least three times more efficient than Fenton reagent and H$_2$O$_2$ as shown in figure 5.13.
Photolytic/Photocatalytic Degradation of Polyvinyl Chloride Plastic Wastes from the Environment

Investigations on Advanced Oxidation Processes as potential environment friendly techniques for the degradation of plastic pollutants

Figure 5.13: Comparative efficiency of TiO$_2$, TiO$_2$ + H$_2$O$_2$, Fenton reagent and PDS for the photodegradation of PVC plastic

Combination of methods ie, (TiO$_2$+H$_2$O$_2$), (TiO$_2$+Fenton), (PDS+H$_2$O$_2$) and (PDS+Fenton) do not lead to any significant enhancement in the degradation of PVC, over what has been achieved in presence of PDS only.

As irradiation progresses, the plastic sheet becomes thinner with localised cracks of various types and ruptured blisters. The photocatalytic degradation of PVC is further demonstrated from the surface morphology of the PVC sheet as seen from its SEM images. Figure 5.14 clearly illustrates that the surface morphology of plastic is severely changed and the technique is effective for the degradation of recalcitrant plastics.
Figure 5.14: SEM images of PVC plastic (a) before, (b) after photolytic treatment using PDS (2000 mg/L), Time: 400 hr and (c) after photolytic treatment using FR (FS: H₂O₂; 80:400 mg/L), Time: 400 hr
The FTIR spectra of the PVC sheet before and after treatment with PDS are shown in figure 5.15 (a) and (b).

(a) Untreated PVC

Typical bands at 2915, 1343, 1244 and 639cm⁻¹ which can be attributed to ν-CH₂ and ν-CH (vibrational absorption), δ-CH₂ and δ-CH (rotational absorption) and ν_c-c (vibrational absorption) respectively are quite evident in the spectra of PVC sheet before treatment. Many of these bands became weak after the photocatalytic treatment indicating degradation.
The IR spectra clearly shows variation in the chemistry of PVC plastic after photolytic degradation, as seen from the appearance of extra bands. Similarly, many of the transmission bands typical of PVC in the range of 620-4000 cm\(^{-1}\) in PVC disappear on photolytic degradation.

It has been proven earlier that PDS is not an effective oxidant of organic compounds under visible light or diffused light [203]. This is reconfirmed again by conducting PVC degradation experiments under identical conditions in the dark, diffused light and UV light. The results show that the degradation is maximum in the presence of UV light (figure 5.16).
In presence of semiconductor mediated photocatalysis PDS is known to enhance the degradation of organic pollutants by trapping the photo-produced electrons, thereby preventing the unproductive electron-hole recombination. In the absence of catalyst also, PDS can lead to the generation of more reactive free radicals and oxidising species such as \( \cdot \)OH and \( \mathrm{SO}_4^- \). The oxidation rate of intermediate compounds can be enhanced and the decrease in \( \mathrm{O}_2 \) in the system during the degradation can be compensated by the PDS.
The mechanism of PVC degradation promoted by PDS may be proposed as follows:

(R = PVC in this case)

\[
S_2O_8^{2-} \rightarrow 2 SO_4^- \quad \text{..................................................} \quad (107)
\]

\[
S_2O_8^{2-} + R \rightarrow 2 SO_4^- + R \quad \text{..................................................} \quad (108)
\]

\[
SO_4^+ + H_2O \rightarrow SO_4^{2-} + H^+ + \cdot OH \quad \text{..................................................} \quad (109)
\]

\[
SO_4^- + R \rightarrow R^- + \text{Products} \quad \text{..................................................} \quad (110)
\]

\[
\cdot OH + R \rightarrow \text{Intermediates} \rightarrow \text{Products} \quad \text{..................................................} \quad (111)
\]

\[
SO_4^+ + R^- \rightarrow \text{Chain termination} \quad \text{..................................................} \quad (112)
\]

\[
SO_4^- + \cdot OH \rightarrow \text{Chain termination} \quad \text{..................................................} \quad (113)
\]

\[
R^- + \cdot OH \rightarrow \text{Chain termination} \quad \text{..................................................} \quad (114)
\]

\[
2 SO_4^- \rightarrow S_2O_8^{2-} \quad \text{(Chain termination)} \quad \text{..................................................} \quad (115)
\]

\[
2 \cdot OH \rightarrow H_2O_2 \quad \text{..................................................} \quad (116)
\]

\[
2 R^- \rightarrow \text{Chain termination} \quad \text{..................................................} \quad (117)
\]

R^- will breakdown after further interactions with the reactive free radicals eventually resulting in the mineralisation of PVC.

The absence of even simple additive effect in the simultaneous presence of PDS and TiO_2 was surprising. However this may be explained as follows based on the general mechanism of semiconductor photocatalysis. Schematic diagram illustrating the mechanism of photocatalysis is given in figure 5.17.
When a semiconductor is irradiated with photons of energy equal to or greater than its band gap energy (3.2 eV in the case of TiO$_2$ as well as ZnO) the photons are absorbed and electron-hole pairs are created [108,112]. These electrons and holes can either recombine or migrate towards the surface participating in several redox reactions eventually leading to the formation of Reactive Oxygen Species (ROS) such as ·OH radicals and H$_2$O$_2$. These transitory ROS can initiate and promote a number of reactions which end up in complete mineralisation of the pollutants into harmless products such as CO$_2$, water and salts as follows:

\[
\text{SC (Semiconductor)} + \text{hv} \rightarrow h^+ + e^- \tag{118}
\]

\[
h^+ + e^- \rightarrow \text{Heat (Recombination)} \tag{119}
\]

\[
h^+ + \text{OH}^- \rightarrow \cdot \text{OH} \tag{120}
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{H}^+ \tag{121}
\]

**Figure 5.17:** Schematic diagram illustrating the principle of semiconductor photocatalysis [194]
Scavenging of conduction band electrons
\[ e^- + O_2 \rightarrow O_2^- \] (122)

Formation of multiple peroxide species
\[ H_2O_2 \rightarrow HO_2^- \] (123)
\[ HO_2^- + e^- + H^+ \rightarrow H_2O_2 \] (124)

PVC + ROS (H_2O_2, O_2^-, HO_2^-, 'OH etc) → Intermediates
\[ \rightarrow H_2O + CO_2 + \text{Salts} \] (125)

In the case of PVC, HCl is one of the by-products of the degradation. The formation of Cl^- is verified experimentally after 400 hr of irradiation when ~7% of PVC has degraded, by using standard AgNO_3 method. However, the formation of HCl is not reflected in any significant decrease in pH, probably because the acid is getting converted to the potassium salt, by reaction with PDS or other potassium compounds in the system. Since Cl^- ions are known to inhibit the photocatalytic activity of many semiconductor oxides, the inability of TiO_2 to enhance the degradation promoted by PDS may be attributed at least partially to this. However results presented in section 5.3.6 show that Cl^- has practically no effect on the PDS promoted degradation of PVC. It is possible that the insitu formed Cl^- may be more active and can hence interact with the catalyst more effectively thereby inhibiting the reactions leading to the degradation of PVC. Other factors to be considered in this context are related to the interactions involving PDS.

\[ TiO_2 \rightarrow h^+ + e^- \] (126)
\[ S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^- \] (127)
\[ SO_4^{2-} + h^+ \rightarrow SO_4^- \] (128)
Thus in presence of TiO$_2$, both SO$_4^{2-}$ and SO$_4^{-}$ are formed from S$_2$O$_8^{2-}$ during irradiation. The former is known to inhibit many photocatalytic degradation reactions promoted by photoactivated TiO$_2$ [204]. SO$_4^{-}$ is a highly reactive oxidant and hence the inhibition by SO$_4^{2-}$ can be more than compensated. However, it is also possible that the highly reactive SO$_4^{-}$ interacts with S$_2$O$_8^{2-}$ in the bulk as well as on the surface.

$$S_2O_8^{2-} + SO_4^{-} \rightarrow SO_4^{2-} + S_2O_8^{-}$$

This results in the formation of less reactive S$_2$O$_8^{-}$ as well as SO$_4^{2-}$ which can function as inhibitors.

The net effect of all these contradictory and complimentary interactions taking place on the surface as well as in the bulk is that the degradation in presence of (TiO$_2$+ PDS) is more or less same as that in presence of PDS only and the photocatalytic activity of TiO$_2$ is neutralised.

The intermediates may go through many reactions before eventual mineralization. The two highly reactive free radical species (\'OH and SO$_4^{-}$) formed from PDS together can more than compensate for the inhibiting factors, if any, caused by the SO$_4^{2-}$ and Cl$^-$ anions.

It is logical to assume that the cavities inside the plastic strip also expand with irradiation. The degradation is faster in the beginning and then slows down with time. The initial faster rate can be attributed to the interaction of reactive oxygen species and/or oxidising species with adjacent polymer chains leading to the degradation. These molecules of the intermediates have to be etched away so that the interaction with
reactive free radicals and consequent degradation can continue. It is also possible that the degradation is initiated by photons attacking the polymer to create excited state followed by chain scission, branching, cross linking and oxidation. The chemical oxygen demand (COD) and biological oxygen demand (BOD) of the water in which the plastic sample was suspended were found to be nil indicating complete mineralisation of pollutants. At the same time the reaction media contains Cl− as indicated by the formation of AgCl precipitate when treated with AgNO₃.

These results clearly illustrate that even highly recalcitrant materials such as PVC plastic can be mineralised by photolysis under suitably optimized conditions and in presence of oxidants.

PVC is also known to undergo degradation under UV irradiation. Impurities or defects present in the plastic sheet can initiate the degradation. Photolysis of PVC will start with the cleavage of C-Cl bond resulting in the generation of PVC radical.

\[ \text{PVC} + \ h\nu \rightarrow \text{PVC}^\cdot \] .................................................................(130)

Once these carbon centered radicals are formed in the polymer chain, they can interact successively with themselves or with reactive oxygen species (ROS) resulting in the formation of carboxyl, carbonyl or hydroxyl groups. Eventually they all get mineralized to CO₂ and H₂O.

\[ \text{PVC}^\cdot + \text{ROS} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{HCl} \] .........................................................(131)

However these are much slower compared to the PDS or PDS/TiO₂ promoted UV degradation of PVC.
5.3.6 Effect of anions and cations

The degradation of PVC results in the formation of chloride ions. Similarly, use of oxidants such as PDS results in the formation of \( \text{SO}_4^{2-} \) ions. The anions may influence the efficiency of photo/photocatalytic processes as has been demonstrated in many earlier studies [170]. Hence the effect of a series of anions which are likely to be present in the environment/water/soil with which the PVC plastic is likely to be in contact when littered, is investigated. Detailed studies were conducted to find the effect of anions and cations on the photocatalytic degradation of PVC plastic under the optimized conditions of other parameters. The effect of various anions on the photodegradation of PVC is shown in figure 5.18. Results show that presence of anions and cations at least in the concentration range studied here does not influence the photocatalytic degradation of PVC plastic. The cation is kept as same; ie Na\(^+\), in all these cases.

![Figure 5.18: Effect of anions on the PDS promoted photocatalytic degradation of PVC](image)

**Figure 5.18:** Effect of anions on the PDS promoted photocatalytic degradation of PVC
Study of the effect of various cations on the photocatalytic degradation shows that the degradation is practically unaffected in the presence of those cations (figure 5.19). In all these cases, the anion is kept the same; ie Cl–.

The results show that K+ has slight enhancing effect. Similar results with K+ cation has been reported earlier also [205].

![Bar chart showing the effect of cations on the photocatalytic degradation of PVC in presence of PDS](image)

**Figure 5.19:** Effect of cations on the photocatalytic degradation of PVC in presence of PDS

If K+ as a cation has enhancing effect on the photocatalytic degradation of PVC, the same should be reflected in the case of PDS also ie PDS with K+ as cation (K₂S₂O₈) must be a better promoter compared to that with Na+ ie, (Na₂S₂O₈). The degradation efficiencies of Na₂S₂O₈ and K₂S₂O₈ are compared and the results are shown in figure 5.20. The results clearly show that K+ as the cation has a positive role in enhancing the degradation of PVC under photolysis.
Photolytic/Photocatalytic Degradation of Polyvinyl Chloride Plastic Wastes from the Environment

Investigations on Advanced Oxidation Processes as potential environment friendly techniques for the degradation of plastic pollutants

Figure 5.20: Comparative efficiency of $\text{K}_2\text{S}_2\text{O}_8$ and $\text{Na}_2\text{S}_2\text{O}_8$ for the Photodegradation of PVC

The effect of cations on the photocatalytic degradation of organics has not been investigated in detail. Even those limited number of reports give conflicting results. Presence of the anions in the salt which have their own inconsistent effect on photolytic processes, depending on concentration, reaction time, light intensity etc is another factor which complicates the salt effect. Extensive investigations under carefully designed conditions, including delineation of anion effect is important in this context. Such an investigation is beyond the scope of the current study and is hence not undertaken in this context of application of photocatalysis in pollution control. However, the possibility of using the mild enhancing effect of $\text{K}^+$ for increasing the efficiency of photodegradation is examined by adding KCl at different concentrations [figure 5.21]. The degradation increases moderately with increase in concentration of $\text{K}^+$ and stabilizes/decreases at higher concentration. The anion is chosen as Cl$^-$ since, it does not have
any inhibiting effect on the degradation [figure 5.18]. The mild increase is not due to Cl\(^-\), as the enhancement is less in the presence of NaCl (figure 5.22). However, the eventual stabilization/decreasing trend may be due to Cl\(^-\) also, as seen from the similarity in the effect at higher concentration of KCl as well as NaCl.

**Figure 5.21:** Effect of concentration of K\(^+\) ions on the photocatalytic degradation of PVC in presence of PDS

**Figure 5.22:** Effect of concentration of Na\(^+\) ions on the photocatalytic degradation of PVC in presence of PDS
5.3.7 Effect of thickness of plastic sheet

One of the parameters which varies widely in the case of plastic sheets is their thickness. Hence the effect of thickness of the plastic sheet on the photocatalytic degradation was studied by taking PVC strips of different thickness. The experiment was done by taking three PVC samples of 1mm, 2mm and 3mm thickness keeping all other parameters constant. The results are presented in table 5.1. Irrespective of the thickness, the actual weight loss is more or less same.

<table>
<thead>
<tr>
<th>Weight of PVC sample (g)</th>
<th>Thickness of PVC sample (mm)</th>
<th>Weight loss in 40 hr (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3333</td>
<td>1</td>
<td>0.063</td>
</tr>
<tr>
<td>4.5672</td>
<td>2</td>
<td>0.065</td>
</tr>
<tr>
<td>6.8923</td>
<td>3</td>
<td>0.064</td>
</tr>
</tbody>
</table>

Table 5.1: Effect of thickness of plastic sheet on the photodegradation of PVC plastic in presence of PDS [PDS]: 2000mg/L

The results show that as long as the surface area of the plastic sheet exposed to UV irradiation is the same the rate of degradation is independent of the thickness of the sheet. This observation is significant for the field application because, the shape/size of the plastic waste is immaterial in the efficiency of the process. Maximum exposure of the surface of the plastic films to the light irradiation is the critical factor.

5.3.8 Effect of combination of pollutants on the degradation of individual components

As PDS was found to be the best oxidiser for the degradation of both LDPE and PVC plastic, the effect of this oxidant on the photodegradation of the pollutants when they are together in the same reaction system was
investigated by keeping the same optimum concentration of catalyst and oxidants as for individual components. The experiment was done in three sets. In all the three cases a suspension of 1400 mg/L TiO$_2$ and 2000 mg/L PDS was used. In the first experimental set up only LDPE strips and in the second case only PVC strips were suspended. Both LDPE and PVC strips were suspended together in the third system. The three sets were irradiated under identical conditions. The results are presented in figure 5.23. The rate of degradation is less in the case of both plastics when they are irradiated together. The effect of combination is less in the case of the relatively faster degrading LDPE. In the case of PVC plastic the degradation is inhibited more in the presence of LDPE. It is also observed that there is only slight increase in the degradation of PVC in the combination with time, in comparison to the system in which only PVC was there (figure 5.24).

![Figure 5.23: Comparative photodegradation of LDPE plastic individually and when in combination with PVC](image)

% weight loss
LDPE alone
LDPE in LDPE+PVC combination
[TiO$_2$]:1400 mg/L
[PDS]:2000 mg/L

Time (hr)
TiO$_2$ as a photocatalyst has only negligible effect on the PDS induced degradation of PVC as demonstrated by earlier results. In view of the inhibition of PVC degradation in presence of LDPE, the possibility of augmenting the degradation of the former in the combination using varying amounts of TiO$_2$ as the photocatalyst is tested. Results are shown in figure 5.25 and 5.26. In the case of PVC plastic individually, the PDS induced degradation was unaffected in the presence of TiO$_2$. However in the combined system (of LDPE + PVC) the degradation of PVC is slightly enhanced in presence of TiO$_2$ (figure 5.25). As expected the enhancement is significant in the case of LDPE. It is possible that the multitude of free radicals present in the system including those formed from LDPE may be assisting the degradation of PVC in presence of TiO$_2$. However, increasing the dosage of TiO$_2$ beyond the earlier optimized
quantity of 1400mg/L does not affect the degradation of PVC or LDPE (figure 5.26).

![Bar chart showing the degradation of LDPE and PVC in the presence and absence of TiO₂.](image)

**Figure 5.25:** Effect of TiO₂ on the degradation of LDPE and PVC plastics when they are present together.

![Bar chart showing the effect of increase in concentration of TiO₂ on the photocatalytic degradation of LDPE and PVC plastics.](image)

**Figure 5.26:** Effect of increase in concentration of TiO₂ on the photocatalytic degradation of LDPE and PVC plastics in combination.
Hence it is clear that the optimum dosage of TiO$_2$ remains the same irrespective whether LDPE and PDS are present individually or in combination. An important observation is that the efficiency of TiO$_2$/PDS is reasonably sustained even when the plastic pollutants are combined together and irradiated. This will be important for the commercial application of the process where many different types of plastic pollutants of all sizes, shapes and chemistry must be treated economically.

5.3.9 Mechanism of the photolytic/photocatalytic degradation of polyvinyl chloride

Under UV irradiation, and in the presence of oxygen and moisture, PVC undergoes dehydrochlorination and peroxidation process with the formation of polyenes [206]. UV energy absorbed by plastics leads to the excitation by photons, which then create free radicals. These free radicals form hydroperoxides in the presence of oxygen and the process is often called photooxidation. In the absence of oxygen also there will be degradation due to the cross-linking process [207].

Various steps involved in the photooxidation of PVC can be described as follows [208-209]:

(1) Formation of polyene radical
(2) Formation of peroxy radical
(3) Formation of PVC radical
(4) Formation of $\gamma$-chloroalkyl peroxy radical
(5) Formation of hydroperoxide groups
(6) Formation of peroxide bridge
(7) Formation of alkoxy radicals
The reactions involved can be presented as in reactions (132)-(141).

\[-(\text{CH}_2\text{CHCl})^- + \text{hv} \rightarrow -(\text{CH}_2^\cdot\text{CH})^- + \cdot\text{Cl} \] .........................(132)

(Formation of polyene and \cdot\text{Cl} radicals)

\[-(\text{CH}_2\cdot\text{CH})^- + \text{O}_2 \rightarrow -(\text{CH}_2(\text{OO}^\cdot)\text{CH})^- \] ..............................(133)

(Scavenging of polyene radical by \text{O}_2 to form peroxy radical)

\[-(\text{CH}_2(\text{OO}^\cdot)\text{CH})^- + -(\text{CH}_2\text{CHCl})^- \rightarrow -(\text{CH}_2(\text{OOH})\text{CH})^- + -(\text{CHCHCl})^- \] ..............................(134)

(Formation of PVC radical by the interaction of PVC with peroxy radical)

\[-(\text{CH}_2(\text{OO}^\cdot)\text{CH})^- + -(\text{CH}_2\text{CHCl})^- \rightarrow -(\text{CH}_2(\text{OOH})\text{CH})^- + -(\text{CH}_2\text{CCl})^- + \text{O}_2 \rightarrow -(\text{CH}_2(\text{OO}^\cdot)\text{Cl})^- \] ..............................(135)

(Formation of \gamma\text{-chlooroalkyl peroxy radical})

\[-(\text{CH}_2(\text{OO}^\cdot)\text{Cl})^- + -(\text{CH}_2\text{CHCl})^- \rightarrow -(\text{CH}_2(\text{OOH})\text{Cl})^- + -(\text{CH}_2\text{CCl})^- \] ..............................(136)

(Formation of hydroperoxide groups by hydrogen abstraction from PVC)

\[-(\text{CH}_2\text{C}(\text{OO}^\cdot)\text{Cl})^- + -(\text{CH}_2\text{CClOOCCl})^- \] ..............................(137)

(Formation of peroxide bridge)

\[-(\text{CH}_2\text{C}(\text{OO}^\cdot)\text{Cl})^- \rightarrow -(\text{CH}_2\text{C}(\text{O}^\cdot)\text{Cl})^- \] ..............................(138)

(Formation of alkoxy radicals)

\[-(\text{CH}_2\text{C}(\text{O}^\cdot)\text{Cl})^- \rightarrow -(\text{CH}_2\text{C(OH)Cl})^- \rightarrow >\text{C}=\text{O} \] ..............................(139)

(Decomposition of alkoxy radical to the corresponding ketone)
Photolytic/Photocatalytic Degradation of Polyvinyl Chloride Plastic Wastes from the Environment

\[(\text{CH}_2\text{C}(\text{O} \cdot \text{Cl}) - \rightarrow \text{C}=\text{O})\] ...............................(140)

(\(\beta\)-scission of alkoxy radical to form the corresponding ketone)

\[-(\text{CH}_2\text{C}(\text{O})\text{Cl}) - \rightarrow -(\text{CH}_2\text{C}(\text{O})\text{Cl})^- + \text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{Cl}^-\text{CHCH}_2\text{Cl}^-\] ...............................(141)

(\(\beta\)-scission of alkoxy radical to form corresponding polyene)

Photolysis of PVC in the presence of \(\text{O}_2\) leads to primary photochemical processes resulting in the formation of excited singlet polynenes. These excited states will then disappear by various routes including the allylic (C-Cl) bond cleavage with the formation of (Cl) radical and polyene radical (eqn.132). The polyene radical which bears no Cl atom in the \(\alpha\)-position is likely to be scavenged by \(\text{O}_2\) to give peroxy radical (eqn.133). The peroxy radical reacts with the (CH\(_2\)) and (CH Cl) groups on PVC resulting in PVC radical (eqn.134). This is followed by the chain-dehydrochlorination of PVC (eqn.134). The peroxy radical attacks the (CH\(_2\)CHCl) group resulting in the formation of radical which possesses no labile \(\beta\)-chlorine (eqn.135) and it is likely to react with (O\(_2\)) to give a \(\Upsilon\)-chloroalkyl peroxy radical (eqn.135). The main oxidation products of PVC are expected to result primarily from various reactions of this radical. There are two major routes for the disappearances of the \(\Upsilon\)-chloroalkyl peroxy radical. The hydrogen abstraction from PVC with the formation of hydroperoxide groups (eqn.136) and the bimolecular interaction, leading to the formation of either a peroxide bridge (termination reaction, eqn.137) or the formation of alkoxy radicals (eqn.138). The most common reaction of alkoxy radicals is the hydrogen abstraction. The \(\alpha\)-chloroalcohol formed by reaction of alkoxy radical with PVC is not stable and will rapidly decompose to the corresponding ketone, (eqn.139). Tertiary
alkoxy radicals are also proved to be stabilized by β–scission. This process involves either (C-Cl) bond cleavage to form ketone or/and (C-C) bond cleavage to form polyene (eqn.140 and eqn.141) [211]. Thus it may be seen that both chlorinated volatile organic compounds as well as oxygenated compounds are formed. The bond energies of C-Cl and C-OH are almost the same [212]. Hence the formation of chlorinated and oxygenated products is controlled by the availability of ‘Cl and ‘OH radicals. In water matrix with excess of water molecules all around, generation of ‘OH radicals will be prominent. These free radicals can compete with ‘Cl in interacting with the PVC molecules and form different types of oxygenated compounds.

In addition to the above sequence of reactions, many other processes will be taking place in the photocatalytic system in presence of TiO₂. As seen in reaction (132) ‘Cl free radicals are formed in the beginning of the process. Both photodegradation and photocatalytic degradation are possible in the system. CHCl₃, COCl₂ and CO₂ are reported from the photocatalytic degradation of PVC [213]. However, in the current study these compounds are not detected, probably because of the limitation of the analytical techniques used to measure small concentrations. Formation of these products shows that the photocatalytic degradation is an oxidation process. The mechanism of the process in presence of TiO₂ can be proposed as follows:

\[ \text{TiOH}^+ + \text{CHCl}_3 \rightarrow \text{TiOH}_2^+ + \cdot \text{CCl}_3 \]  \hspace{1cm} (142)

\[ \text{Ti}^{IV} \text{OH}^- + \cdot \text{CCl}_3 + \text{O}_2 \rightarrow \text{Ti}^{IV} \text{OH}_2^- + \cdot \text{O}_2\text{CCl}_3 \]  \hspace{1cm} (144)
Photolytic/Photocatalytic Degradation of Polyvinyl Chloride Plastic Wastes from the Environment

$2 \cdot \text{O}_2\text{Cl}_3 \rightarrow 2\cdot \text{OCCl}_3 + \text{O}_2$ ...................................................(145)

$\cdot \text{OCCl}_3 + \text{HO}_2^* \rightarrow \text{Cl}_2\text{COH} + \text{O}_2$ ...................................................(146)

$\text{Cl}_2\text{COH} \rightarrow \text{Cl}_2\text{CO} + \text{H}^+ + \text{Cl}^-$ .........................................................(147)

$\text{Cl}_2\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{Cl}^-$ .....................................................(148)

The general mechanism of photocatalysis involving the formation of reactive ‘OH and other ROS is shown in figure 5.17, section-5.3.5. The highly reactive ROS can interact with PVC and various photogenerated radicals formed from it resulting in eventual degradation/mineralisation.

Thus eventually the recalcitrant polymer is irreversibly degraded to safer products. The mechanism of PVC degradation in presence of PDS, $\text{H}_2\text{O}_2$ and Fenton reagent is discussed in respective sections.

5.4 Conclusions

Semiconductor photocatalysis mediated by $\text{TiO}_2$ and/or peroxydisulphate is found to be a promising method for the safe removal of solid phase PVC plastic pollutants from the environment. Acidic pH enhances the degradation. However, due to economic and environmental concerns, this may not be a preferred option. Hence reaction parameters for optimum degradation efficiency were identified keeping pH at the natural harmless range of 5.5-7. Oxidants such as $\text{H}_2\text{O}_2$, Fenton reagent and peroxydisulphate (PDS) enhance the degradation. PDS is at least three times more efficient than the other oxidants. $\text{TiO}_2$ has no additional effect on the degradation of PVC plastic in the presence of Fenton reagent and PDS. Optimum concentration of PDS could achieve over 7% of PVC...
mineralisation in 400hr time. Complete mineralisation of PVC into CO₂, H₂O and salts are confirmed by the absence of any suspended matter as well as COD and TOC in water. The presence of salts (anions and cations) commonly present in water does not influence the photocatalytic degradation of PVC plastic. The degradation is not affected by the thickness of the PVC sample, as long as the light exposed surface area remains the same. Combination of LDPE and PVC in the same reaction system gives almost the same rate of degradation for both as in the case of systems with only individual components. However, in presence of TiO₂ photocatalyst, the degradation of PVC in the combination is more compared to the individual system. The study demonstrates that photocatalysis mediated by TiO₂ and/or peroxydisulphate offers good potential for the safer mineralisation of one of the worst environmental pollutant of the day, i.e. PVC plastics.