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Enhancement of Semiconductor Mediated Photocatalytic Removal of Polyethylene Plastic Wastes from the Environment by Oxidizers

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Abstract

Plastics have become an essential ingredient of modern life with wide range of applications. At the same time the 'white pollution' caused by plastic wastes is a major environmental problem due to their recalcitrant nature. Even the simplest form of plastics, i.e., polyethylene is strong and highly durable and takes upto 1000 years for natural degradation in the environment. Current study reveals that photocatalysis can be used successfully as an Advanced Oxidation Technique for the slow but steady degradation of polyethylene plastics (PEP). Semiconductors such as ZnO and TiO_2 *assist the photodegradation of PEP through the generation of highly reactive free radicals which interact with the pollutant.* TiO_2 *is at least 20% more efficient than ZnO as a photocatalyst in this respect. The process is pH dependent and acidic condition favours the degradation. Oxidizing agents such as* H_2O_2 *and peroxydisulphate (PDS) accelerate the semiconductor catalysed degradation. The enhancement depends on the concentration of the oxidizer and stabilises at an optimum range. Critical parameters for optimum efficiency for the degradation of PEP are identified and evaluated. A tentative mechanism for the degradation is also proposed based on the observations.*

Keywords: Photocatalysis, zinc oxide, titanium dioxide, polyethylene plastic, oxidizers.

Introduction

Polyethylene is a thermoplastic made up of long chain of monomer ethylene. Based on the degree of polymerization, polyethylene plastics (PEP) are of two types: Low density polyethylene (LDPE) and High density polyethylene (HDPE). Crystallinity of LDPE is low at ~ 55% and has a density in the range of 0.910- 0.925g/cm^3. LDPE form is used to make carrier bags, bottles, toys, mugs and a variety of other less expensive daily use products. It is tough and flexible, is a good insulator of heat and electricity and shows considerable resistance towards acid, alkali and salt solutions. Extensive use of LDPE plastics with no safer or convenient disposal avenues has been creating serious environmental hazard. New inexpensive and safer technologies have to be developed for the degradation of these plastic wastes. Heterogeneous photocatalysis is an Advanced Oxidation Process (AOP), widely investigated for the degradation of organic pollutants in water and air[1-6]. The basic mechanism of photocatalysis involving hydroxyl radicals has also been well established[7,8].

Semiconductor oxides such as TiO_2 and ZnO and their modifications by doping, immobilizing, metal deposition, dye sensitization etc. are the most widely used photocatalysts[9-11]. Among the semiconductors TiO_2 is the most widely used photocatalyst 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 a larger fraction of solar spectrum compared to the latter[12-17]. Basic mechanism of semiconductor photocatalysis involves photo excitation of the valence band electrons to the conduction band thereby creating electron deficiency or hole in the valence band. Dioxygen in the system, on the surface as well as in the bulk, serves as a sink for conduction band electron forming superoxide $O_2^{\cdot -}$ which leads to the formation of a number of Reactive Oxygen Species (ROS)[4,5,7-9]. Holes in the valence band can react with water molecules or hydroxide anion to form OH radicals. The holes can also interact with adsorbed organic donors leading to their degradation and possible mineralization.

In spite of the severe hazards caused by PEP to the environment and ecology, the number of research studies, especially Advanced Oxidation Processes (AOP) aimed at developing safer technologies for their disposal is relatively few. In the present study the possibility of using photocatalysis mediated by TiO_2 and ZnO for the degradation of PEP is investigated. The effect of various reaction parameters including pH and presence of oxidizing agents on the photocatalytic degradation of PEP in TiO_2 suspensions is also examined and optimized.

Material and Methods

ZnO (>99.9%) and TiO_2 (>99.9%) used in the study were supplied by Merck India Limited. The BET surface areas of TiO_2 and ZnO were 15 and 12 m^2/g respectively. The average particle size of both was ~10 μm as determined by Scanning

Electron Microscopy (SEM). Typical SEM of ZnO and TiO_2 are shown in figure-1. All other chemicals/ reagents used were of AnalaR grade or equivalent unless indicated otherwise.

Typical PEP strips made from throwaway type used carry-bags were used in the study. The strips were washed thoroughly, dried and then fully immersed in aqueous suspension of TiO_2/ZnO and irradiated with frequent mixing in a multi lamp photo-reactor (Heber Scientific India) which consisted of a lamp-housing with eight UV lamps of 8 W each. The primary wavelength of the lamps was 365 nm. After specific intervals the plastic strips were taken out, washed well to remove sticking particles of catalyst, if any, and dried at room temperature in air flow until constant weight is reached. The weight loss, change in physical appearance including visible decrease in thickness, increased crumbling, periodic SEM imaging and tensile strength measurements were used to identify the destruction of PEP subjected to irradiation under different conditions.

Results and Discussion

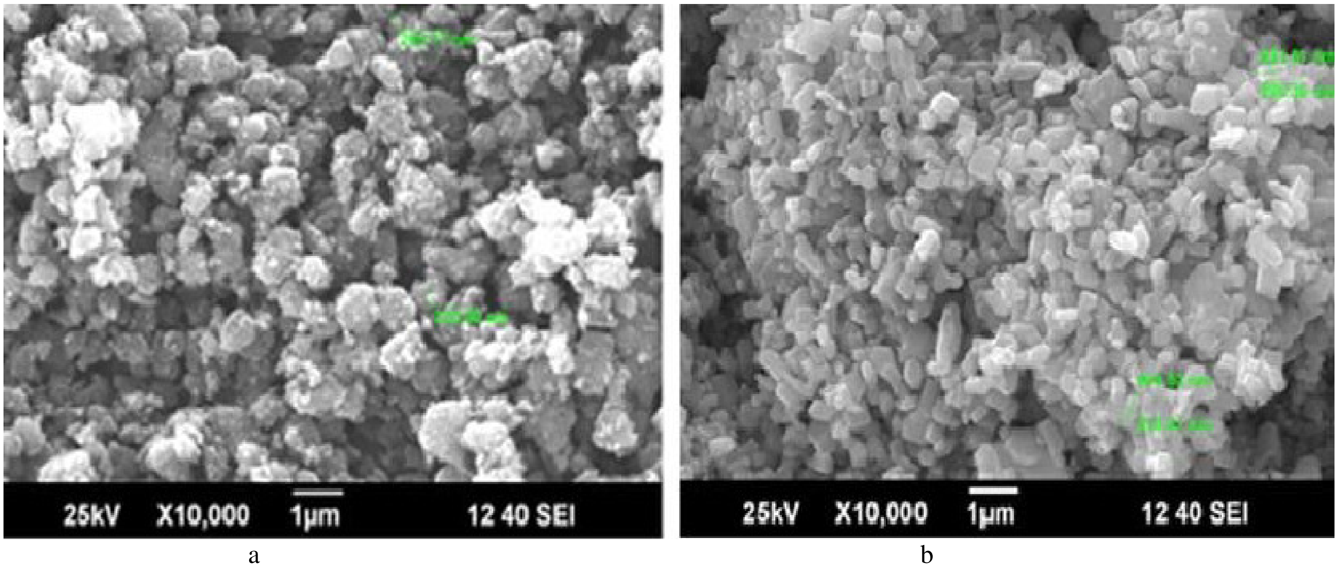
Investigations on the photocatalytic degradation of PEP using ZnO and TiO_2 catalysts under identical conditions showed that no significant degradation took place in the absence of UV light or the catalyst suggesting that both catalyst and light are essential to effect degradation. The ultimate reaction products were expected to be CO_2 and H_2O formed by the degradation of polyethylene. Since the amount of CO_2 formed is very small, its quantitative estimation is difficult. The Total Organic Carbon (TOC) content in water is ‘nil’ indicating complete mineralisation of the PEP as well as the intermediates formed.

Effect of Catalyst Dosage: Comparative efficiency of TiO_2 and ZnO at various loadings for the degradation of PEP is shown in figure-2.

As seen from the figure, the optimum loading for ZnO and TiO_2 is 1400 mg/L. Beyond the optimum loading, the light photon absorption coefficient decreases radially and the degradation slows down. However such light 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[18]. Excess catalyst particles lead to screening of light which reduces the effective surface area of the semiconductor being exposed to illumination resulting in decreased photocatalytic efficiency. Since TiO_2 is more efficient for the degradation compared to ZnO under identical condition all further investigations in this report were carried out using the former at the optimized loading as above, unless mentioned otherwise.

Effect of pH: The photocatalytic degradation of organics is reported to be generally dependent on the pH value of the solution. Our studies using a variety of substrates on ZnO, TiO_2 and their combination also confirmed this[19,20]. Hence the effect of pH on photocatalytic degradation of PEP was investigated in the range 2.5-10. The pH of the suspension was adjusted before irradiation and was not controlled thereafter. The results are presented in figure-3.

The degradation is more efficient in the acidic region even in the absence of the catalyst. However at the natural pH of the catalyst suspension (~ 6.5-7), noticeable degradation takes place only in the presence of the catalyst. 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 noted in presence of TiO_2 and light.



a b

Figure-1
SEM image of (a) TiO_2 and (b) ZnO

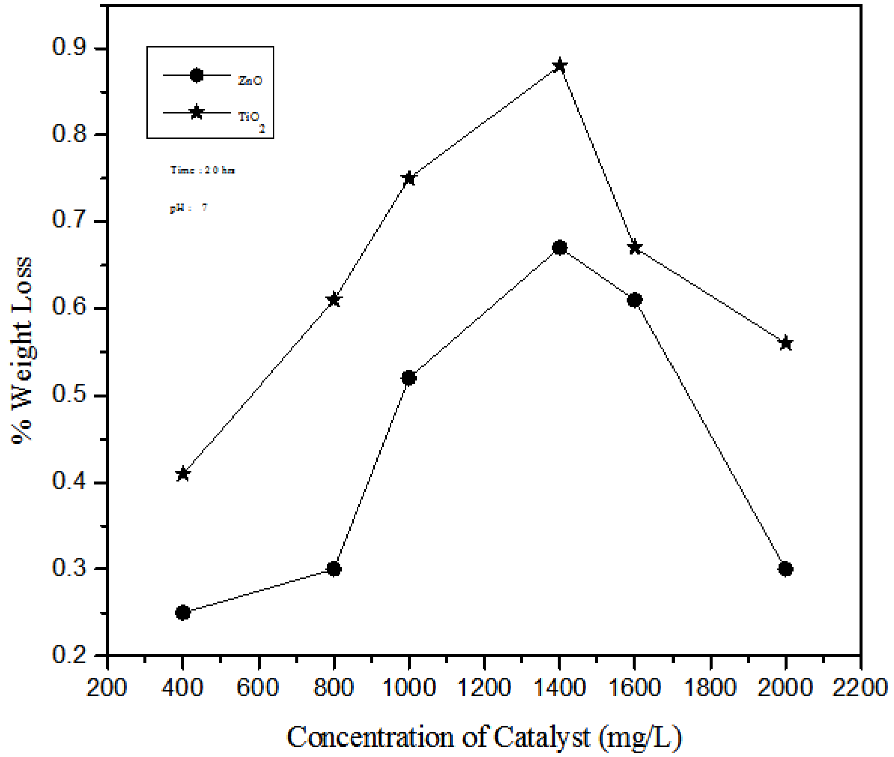


Figure-2
Comparative efficiency of TiO_2 and ZnO for the photocatalytic degradation of PE plastic

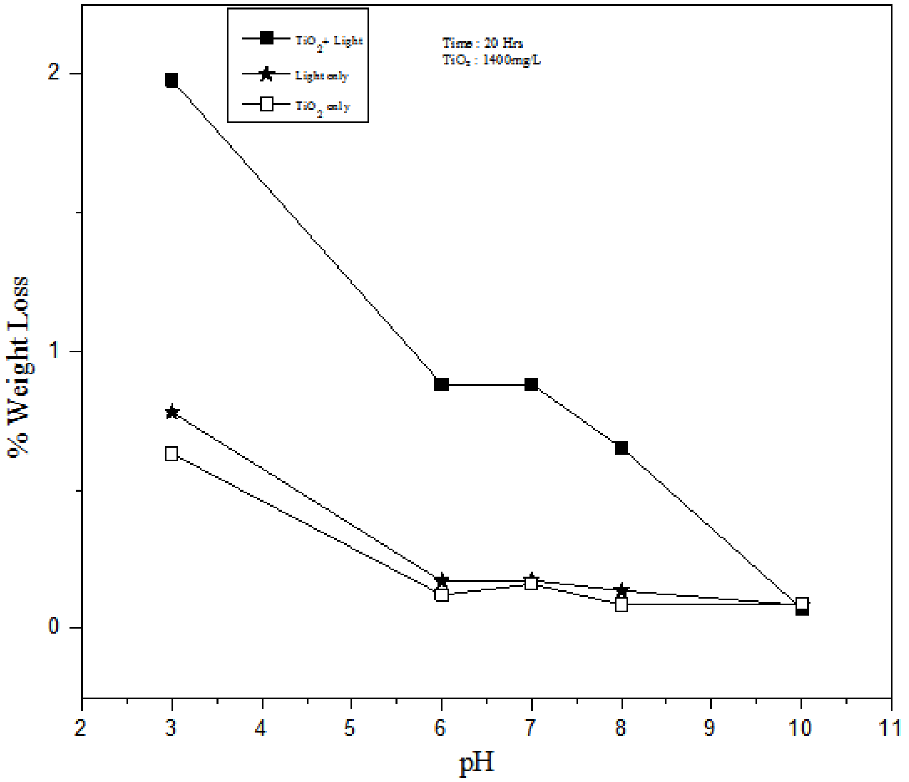


Figure-3
Effect of pH on the degradation of PE plastic

Effect of oxidizers on the degradation: Hydrogen peroxide is detected as a byproduct/intermediate in the photocatalytic degradation of organic pollutants. It has also been reported that the H_2O_2 thus formed undergoes simultaneous decomposition resulting in periodic increase and decrease in its concentration[19,20]. In the present instance of photocatalytic degradation of plastics also, H_2O_2 is detected in the reaction medium. However, its concentration is very small (< 2 mg/L) and is hence not followed up. The reactive free radicals such as $^{\cdot}OH$ and $HO_2^{\cdot}$ formed from H_2O_2 decomposition often have a positive effect on the degradation of organics. Thus added H_2O_2 enhances the decomposition of many pollutants. However, instances of inhibition of degradation by H_2O_2 also have been reported. Our earlier studies have shown that peroxydisulphate (PDS) can also serve as accelerator for the degradation of pesticides and dyes[15]. In view of these, the effect of addition of H_2O_2 and PDS on the degradation of PEP is investigated. The results are plotted in figure-4.

In both cases, the degradation of PEP is enhanced and the enhancement continues even after longer periods of irradiation. PDS is much better oxidant compared to H_2O_2. The effect is concentration- dependent with higher concentration favoring increased degradation as shown in figure-5.

H_2O_2 enhances the degradation upto 1500 mg/L concentration while the optimum in the case of PDS is 2000 mg/L under the current reaction conditions. Above this optimum concentration the degradation of PEP is either stabilised or slightly decreased. The general mechanism of semiconductor photocatalysis is illustrated in figure-6.

When a semiconductor is irradiated with photons of energy equal 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[1,2]. 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 $^{\cdot}OH$ radicals and H_2O_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:

$\text{Semiconductor} + h\nu \rightarrow h^+ + e^-$ (1)
$h^+ + e^- \rightarrow \text{Heat}$ (2)
$O_2 + e^- \rightarrow O_2^{-\cdot}$ (3)
$O_2^{-\cdot} + 2H^+ + e- \rightarrow H_2O_2$ (4)
$h^+_{VB} + H_2O \rightarrow H^+ + {}^{\cdot}OH$ (5)
${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$ (6)
$h^+_{VB} + OH^- \rightarrow {}^{\cdot}OH$ (7)
$\text{Pollutant} + \text{ROS } (H_2O_2, O_2^-, HO_2^{\cdot}, OH^{\cdot} \text{ etc})$
$\text{Intermediates} \rightarrow H_2O + CO_2 + \text{Salts}$ (8)

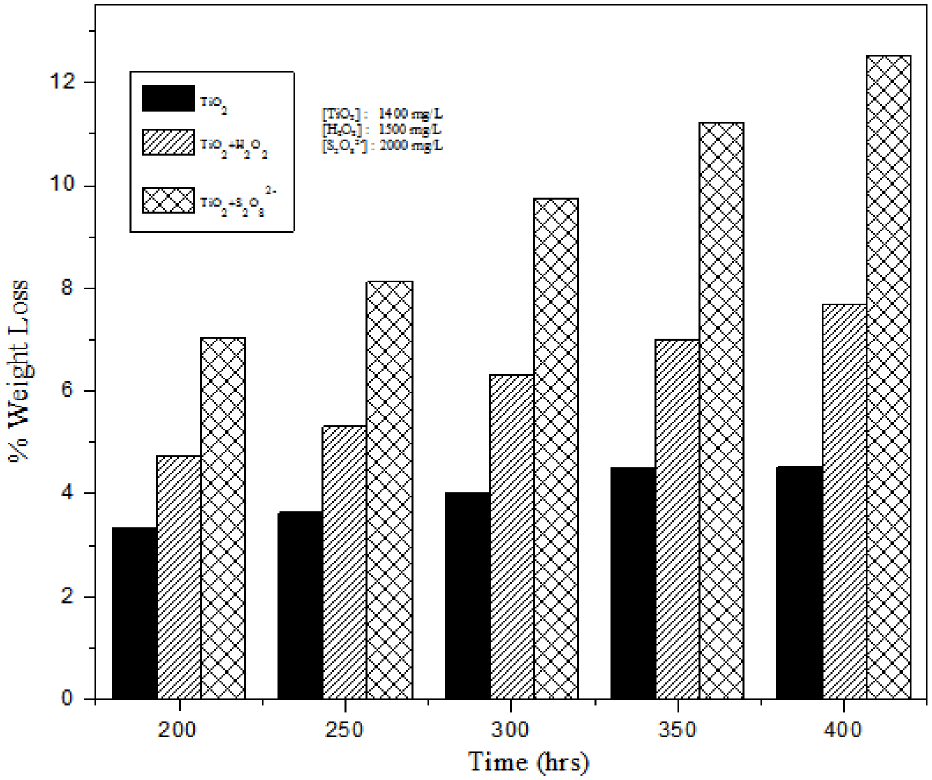


Figure-4

Comparative efficiency of H_2O_2 and $S_2O_8^{2-}$ for the photocatalytic degradation of PE plastic on TiO_2

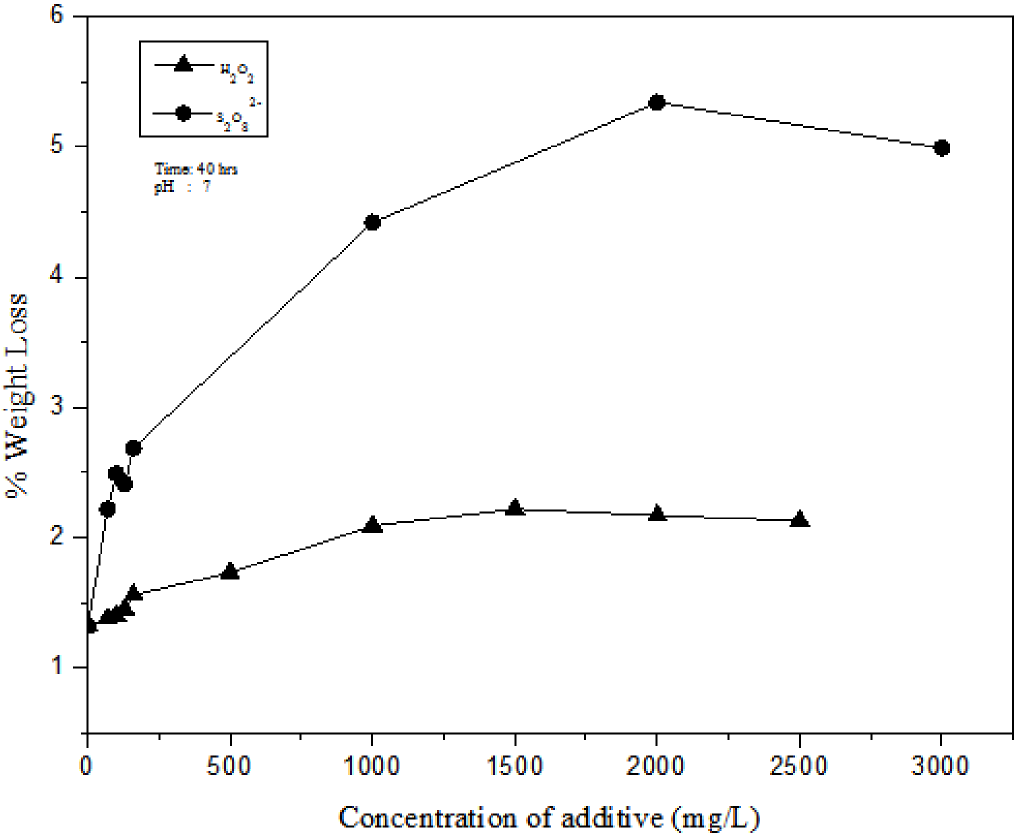


Figure-5
Effect of concentration of H_2O_2 and $S_2O_8^{2-}$ on the photocatalytic degradation of PE plastic on TiO_2

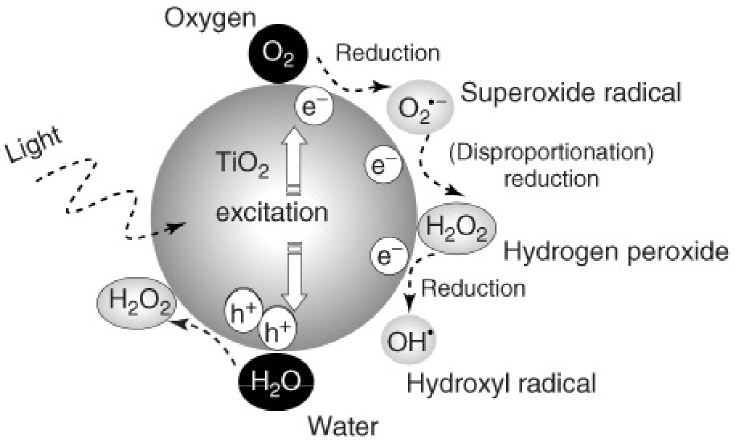


Figure-6
Mechanism of TiO_2 photocatalysis showing formation of $^{\cdot}OH$ and H_2O_2[4]

H_2O_2 is known to decompose under photocatalytic conditions forming more reactive $^{\cdot}OH$ and $HO_2^{\cdot}$ radicals as in reactions 9 and 10. Further H_2O_2 itself is a good electron and hole acceptor capable of preventing the recombination of photogenerated electrons and holes on the surface.

$$H_2O_2 + H^+ + e^- \rightarrow {}^{\cdot}OH + H_2O \quad (9)$$

$$H_2O_2 + {}^{\cdot}OH \rightarrow HO_2^{\cdot} + H_2O \quad (10)$$
$$H_2O_2 + 2h^+_{VB} \rightarrow O_2 + 2H^+ \quad (11)$$
$$H_2O_2 + .OH/h^+_{VB} \rightarrow HO_2^{\cdot} + H_2O/H^+ \quad (12)$$
$$HO_2^{\cdot} + .OH/h^+_{VB} \rightarrow O_2 + H_2O/H^+ \quad (13)$$

Hence the degradation is enhanced in presence of added H_2O_2. However at higher concentration of H_2O_2 the reactive free radicals as well as the electrons and holes interact more with it and less with the pollutant. This leads to stabilization or even decrease in the degradation of PEP. The concentration effect of H_2O_2 on the photocatalytic degradation of organic pollutants was reported by other workers also[21,22].

The TiO_2 catalysed photodegradation of PPE is almost doubled in the presence of even smaller concentration of PDS (5% of TiO_2) as in figure 5. At the optimized concentrations of the oxidants, PDS is at least three times more efficient than H_2O_2. The mechanism of enhancement in PEP degradation by PDS may be proposed as follows:

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\cdot -} \qquad (14)$$

SO_4^{2-} gets adsorbed on the surface and interacts with the photoproduced holes forming reactive sulphate radicals as in reaction-15.

$$H^+ + SO_4^{2-} \rightarrow SO_4^- \qquad (15)$$

Since S is a strong oxidizing agent, the sulphate radical (Reduction potential of $SO_4^{\cdot -}$ = 2.6 V) can accelerate the degradation process according to reactions 16 and 17:

$$SO_4^{-\cdot} + H_2O \rightarrow SO_4^{2-} + {}^{\cdot}OH + H^+ \qquad (16)$$
$$SO_4^{-\cdot} + \text{Pollutant} \rightarrow SO_4^{2-} + \text{Intermediate} \rightarrow$$
$$SO_4^{2-} + CO_2 + \text{Salts} \qquad (17)$$

The intermediate may go through many reactions before eventual mineralization. As seen in reaction 16, extra ${}^{\cdot}OH$ radicals which can enhance the degradation of the pollutant are also formed in presence of PDS. The two highly reactive free radical species (${}^{\cdot}OH$ and $SO_4^{\cdot -}$) together can more than compensate for the inhibition, if any, caused by the depletion of surface sites taken up by the sulphate ions.

SEM images of typical plastic strips before and after photocatalytic treatment are shown in figure-7.

The figure clearly illustrates that the surface morphology of plastic is severely changed and the technique is effective for the degradation of recalcitrant plastics. As irradiation progresses, the plastic sheet becomes thinner, crumbles and breaks. Over 10% of PEP mineralisation could be achieved in 300 hr time in presence of PDS as oxidizer and TiO_2 as photocatalyst.

It is logical to assume that the cavities inside the plastic film also expand with irradiation and the photocatalytic degradation happens both on the surface and inside the film simultaneously. The holes generated and the O_2^- participate in the degradation directly as well as through various radicals generated as follows:

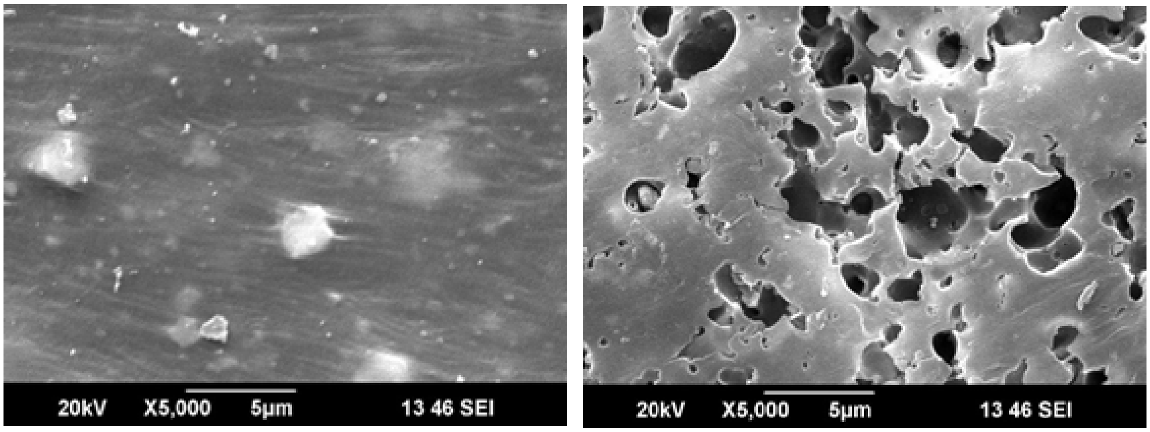
$$H^+ + \text{-}(CH_2CH_2)\text{-} \rightarrow \text{-}(CH_2CH_2)\text{-}^+ \qquad (18)$$
$$\text{-}(CH_2CH_2)\text{-}^+ + O_2^- \rightarrow \text{-}({}^{\cdot}CHCH_2)\text{-} + HO_2 \qquad (19)$$

$HO_2^{\cdot}$ radicals combine to form H_2O_2 which in turn can photodecompose to yield ${}^{\cdot}OH$ radicals.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (20)$$
$$H_2O_2 + h\nu \rightarrow 2{}^{\cdot}OH \qquad (21)$$

The degradation is faster in the beginning and it slows down with time. This is similar to the observations by Shang etal[23] who demonstrated that photocatalytic degradation of polystyrene plastic and evolution of CO_2 and volatile organic compounds under fluorescent light deteriorate gradually. The initial faster rate can be ascribed to the interaction of reactive oxygen species with adjacent polymer chains. These molecules have to be etched away so that the catalyst surface is available for interaction with more molecules and generation of reactive free radicals. 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[24]. During the irradiation, the OH radicals can attack the polymer as follows:

$$\text{-}(CH_2CH_2)\text{-} + {}^{\cdot}OH \rightarrow \text{-}(CH_2{}^{\cdot}CH)\text{-} + H_2O \qquad (22)$$
$$\text{-}(CH_2{}^{\cdot}CH)\text{-} + {}^{\cdot}OH \rightarrow \text{-}({}^{\cdot}CH{}^{\cdot}CH)\text{-} + H_2O \qquad (23)$$



(a) (b)

Figure-7

SEM images of polyethylene plastic (a) before and (b) after photocatalytictreatment using TiO_2 (1400 mg/L) and $S_2O_8^{2-}$ (2000 mg/L), Time: 300 hours

The carbon centered radicals thus formed react with more O_2 leading to chain cleavage and production of new reactive radicals as shown below[23,25].

$$\text{-(CH}_2{}^{\cdot}\text{CH)-} + O_2 \rightarrow \text{-(CH}_2\text{(OO}^{\cdot}\text{)CH)-} \quad (24)$$

$$\text{-(}^{\cdot}\text{CH}^{\cdot}\text{CH)-} + O_2 \rightarrow \text{-(CH(OO}^{\cdot}\text{)CH)-} \quad (25)$$

$$\text{-(CH}_2\text{(OO}^{\cdot}\text{)CH)-} + \text{-(CH}_2\text{CH}_2\text{)-} \rightarrow \text{-(CH}_2\text{(OOH)CH)-} + \text{-(CH}_2{}^{\cdot}\text{CH)-} \quad (26)$$

$$\text{-(CH}_2\text{(OOH)CH)-} \rightarrow \text{-(CH}_2\text{OCH)-} + {}^{\cdot}\text{OH} \quad (27)$$

$$\text{-(CH}_2\text{OCH)-} + O_2 \xrightarrow{\text{Catalyst} + h\nu} \underset{\text{HCHO, HCOOH etc}}{\text{Intermediates such as}} \xrightarrow{\text{Catalyst} + h\nu} CO_2 + H_2O \quad (28)$$

The intermediates are not detected in water indicating that they are getting degraded faster than the plastic. Absence of any TOC in water in which the plastic strip was suspended also confirms this.

Conclusion

Semiconductor photocatalysis mediated by TiO_2 is found to be a promising method for the safe removal of polyethylene plastic pollutants. Acidic pH enhances the degradation. However, due to economic and environmental concerns, this possibility is not explored and reaction parameters for optimum degradation efficiency were developed keeping pH at the natural harmless range of 6-7. H_2O_2 and peroxydisulphate enhance the degradation and the latter is at least three times more efficient than the former. Optimum concentration of peroxydisulphate in presence of TiO_2 as photocatalyst could achieve over 10% of PEP mineralisation in 300 hr time. The technique offers good potential for the safer mineralisation of one of the worst environmental pollutant of the day, i.e. polyethylene plastics.

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References

1. Herrmann J.M., Heterogeneous Photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants, *Catal. Today.,* **53**, 115-129 **(1999)**
2. Hoffmann M., Martin S., Choi W. and Bahnemann D., Environmental applications of semiconductor catalysis, *Chem. Rev*., **95**, 69-96 **(1995)**
3. Devipriya S. and Yesodharan S., Photocatalytic degradation of pesticide pollutants in water, *Solar Energy Mater and Solar Cells,* **86**, 309-348 **(2005)**
4. Nosaka Y and Nosaka A., in Photocatalysis and Water Purification, First Edition, Pichat. P. Ed., Wiley-VCH Verlag GmbH and Co., 1-24 **(2013)**
5. Pelaez M., Nolan N.T., Pillai S.C., Seery M.K., Falaras P., Kontos A.G., Dunlop P.S.M., Hamilton J.W.J., Byrne J.A., O'Shea K., Entezari M.H. and Dionysiou D.D., *Appl. Catal B: Environ*., **125**, 331-349 **(2012)**
6. Ollis D.F., Pichat P. and Serpone N., TiO_2 photocatalysis: 25 years, *Applied Catalysis B: Environ.*, **99** 377-387 **(2010)**
7. Turchi C.S. and Ollis D.F., Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attacks, *J. Catal.,* **122**, 178-192 **(1990)**
8. Mathews R.W., Phto-oxidation of organic material in aqueous suspensions of titanium dioxide, *Wat. Res.,* **20**, 569-578 **(2011)**
9. Wu C.G., Chao C.C. and Kuo F.T., Enhancement of the photocatalytic performance of TiO_2 catalysts via transition metal modification, *Catal. Today,* **97(23),** 103-112 **(2004)**
10. Sakthivel S., Shankar M.V., Palanichamy M., Arabindoo A., Bahnemann D.M. and Murugesan B.V., Enhancement of photocatalytic activity by metal deposition: characterization and photonic efficiency of Pt, Au, and Pd deposited on TiO_2 catalyst, *Wat. Res.,* **38 (130),** 3001-3008 (**2004**)
11. Pellegrin J.Y., Le Pleux L, Blart L.E., Renaud A., Chavilion B., Szuwarski N., Boujitita M., Cario L., Jobic S., Jacquemin D. and Odobel F., Ruthenium polypyridine complexes as sensitisers in NiO based p-type dye-sensitized solar cells: Effects of the anchoring groups, *J Photochem. Photobiol. A-Chem.*, **219(2)**, 235-242 **(2011)**
12. Sakthivel S, Neppolian B, Shankar M.V, Arabindoo B, Palanichamy M and Murugesan V., Solar photocatalytic degradation of azodye: Comparison of photocatalytic efficiency of ZnO and TiO_2, *Solar Energy Mater. and Solar Cells.,* **77**, 65-82 **(2003)**
13. Devipriya S.P and Suguna Yesodharan., Solar photocatalytic removal of chemical and bacterial pollutants from water using Pt/TiO_2-coated ceramic tiles, *Int J Photoenergy, Article* ID 970474 **(2012)**
14. Lam SM, Sin JC, Abdullah A.Z and Mohamed A.R., Degradation of wastewaters containing organic dyes photocatalysed by zinc oxide: a review, *Desalination and Water Treatment*, **41**, 131-169 **(2012)**
15. Shibin O.M, Rajeev B, Veena V, Yesodharan E.P and Suguna Yesodharan, ZnO photocatalysis using solar energy for the removal of trace amounts of Alfa-methylstyrene, Diquat and Indigo Carmine from Water, *J Adv. Oxid. Technol.*, **17**, 297-304 **(2014)**
16. Sindhu Joseph, Jyothi K.P., Devipriya S.P., Suguna Yesodharan and Yesodharan E.P., Influence of reaction

intermediates on the oscillation in the concentration of insitu formed H2O2 during the photocatalytic degradation of phenol pollutant in water on semiconductor oxides, *Res. J. Recent. Sci.*, Intermediates **2**, 82-89 **(2013)**

17. Hariprasad N, Anju S.G., Yesodharan E.P. and Suguna Yesodharan., Sunlight induced removal of Rhodamine B from water through semiconductor photocatalysis: Effects of adsorption, reaction conditions and additives, *Res. J. Mater. Sci.,* **1(14)**, 9-17 **(2013)**

18. He Y., Grieser F and Ashokkumar M., The mechanism of sonophotocatalytic degradation of methyl orange and its products in aqueous solutions, *Ultrason. Sonochem.*, **18**, 974–980 **(2011)**

19. Jyothi K.P., Suguna Yesodharan and Yesodharan E.P., Ultrasound, Ultraviolet light and combination assisted semiconductor catalysed degradation of organic pollutants in water: Oscillation in the concentration of hydrogen peroxide formed insitu, *Ultrason. Sonochem.*, **21**, 1787-1796 **(2014)**

20. Anju S.G, Suguna Yesodharan and Yesodharan E.P., Zinc oxide mediated sonophotocatalytic degradation of phenol in water, *Chem. Eng. J.*, **189-190**, 84-93 **(2012)**

21. Evegenidou E., Fytianos K and Poulios I., Semiconductor-sensitized photodegradation of dichlorvos in water using tiO2 and ZnO as catalysts, *Appl. Catal B : Environ.*, **59**, 81-89 **(2000)**

22. Malato S., Blanco J., Maldonado M.I., Fernandez-Ibanez P and Campos A., Optimising solar photocatalytic mineralization of pesticides by adding inorganic oxidising species: application to the recycling of pesticide containers, *Appl. Catal B: Environ.*, **28**, 163-174 **(2000)**

23. Shang J, Chai M and Zhu Y., Photocatalytic degradation of polystyrene plastic under fluorescent light, *Environ Sci. Technol.*, **37**, 4494-4499 **(2003)**

24. Crawford K.D and Hughes K.D., Rapid formation and spectroscopic observation of polystyrene conjugation in individual micron-diameter particles with visible radiation, *J Phys. Chem., B* **101**, 864-870 **(1997)**

25. Wells R.K., Royston A. and Badyal J.P.S., Direct evidence for the generation of phenyl radicals and cross linking during the photolysis of polystyrene film, *Macromolecules,* **27**,7465-7468 **(1994)**