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Treatment of Plastic Wastes by UV Catalyzation and *Aspergillus Niger*

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Abstract—*Waste polyethylene may be minimized by the specific bacterial/fungal route, but slow rate of biodegradation is the major drawback in the implementation of bacterial/fungal route in the polyethylene degradation. Standard plastics degrade rapidly by photo-degradation. Long chain polyethylene is collapsed into microscopic fragments by UV rays in presence of TiO_2 catalyst with ascorbic acid as a promoter. Rate of polyethylene degradation is increased by 15-17 times by adding ascorbic acid. Further, UV degraded plastic is decomposed by the bacterial/fungal route. Aspergillus Niger is the most common fungi used in the biodegradation of polyethylene which works effectively under low pH. So, use of ascorbic acid in the UV degradation attracts the biological route with Aspergillus Niger. Potato dextrose agar (PDA) plate methods are used for the growth and isolation of Aspergillus Niger. The optimum operating temperature (35^oC) of Aspergillus Niger is determined by the growth study. Further, Aspergillus Niger is acclimatized by gradual transfer of UV degraded plastics with PDA medium. Approximately, 10% and 35% of polyethylene degradation are noted after two months treatment with the UV rays and 1 month with fungal treatment (after treatment with UV rays for two months). This technique may be used as an alternative of chemical/physical decomposition of polyethylene and in the minimization of other pollutants available in the effluents. Fungal/biological route also minimizes the environmental pollution, chemical contamination generated during other treatments.*

1. INTRODUCTION

Plastic products have become an indispensable part of our lives. It is produced on a very huge scale and its production crosses the 150 million tons per year globally. Plastics mainly LDPE are used on a large scale for various purposes and has a wide range of applications in packaging, shopping and garbage bags, clothing, toys, containers, other households and industrial products. It is a versatile alternative to other materials which is economically feasible due to its unique features like they are resistant to corrosion, possess low thermal and electrical conductivity, have low toxicity, is generally lighter, used as a shock resistance, resistant to water and many more. These are the attractive qualities that lead us, around the world, to such a voracious appetite and over consumption of plastic goods. But, some of its characteristics have lethal consequences. It is a fact that plastics are non-biodegradable, hence remains on the landscape and pollutes it for the several years. Recycling is considered as a solution to disposal of plastic wastes, but it needs to be considered that the recycled plastics are more hazardous to the environment than the virgin products. This is so because additional colours, additive stabilizers, flame retards etc. are mixed during recycling. Moreover, the virgin plastic can be recycled only 2-3 times, so the plastic waste disposal and management are still a major problem in the country [1].

Plastic wastes are dumped indiscriminately in the landfills which makes the land infertile due to their barrier properties. Burning of plastics is not a solution to the disposal issues as this generates toxic emissions such as Carbon Monoxide, Chlorine, Hydrochloric acid, Dioxin, Furans, Amines, Nitrides, Styrene Benzene, 1,2-butadiene, CCl_4 and acetaldehyde. Littered plastic wastes choke the drains, may cause flood during monsoons and give an unaesthetic scenario in the city. The mixed garbage, plastic mixed with other wastes, poses a big challenge in waste processing. Plastic waste disposal and degradation has been a major topic of discussion in the field of research in the past decades. Many ideas and methods have been proposed for solving this issue. Plastic degradation can be broadly grouped into three major domains, which includes photo-degradation, biological degradation and chemical degradation.

Thereafter, numerous methodologies have been adopted to remove the ill effects and in the contemporary world, we are heading towards using bio-plastics, degradable PET bottles, using plastics in road making, as a fuel etc. but then too, it did not ensure a proper disposal of it and is still a matter of great concern to us to the plastics which has already been formed and will take more than hundreds of years to degrade. These are harmful to the flora and fauna and carcinogenic too. It also hinders the sustainable development of a country by increasing the pollutions levels because of its huge impact [2].

Since, plastics mainly LDPE like polyethylenes are huge in number and consists of polymeric chains which takes longer time for it to degrade. So, by increasing the rate of degradation, we can solve the problem to a greater extent to

ensure a proper disposal. Many ideas and methods have been proposed for solving this issue. Plastic degradation can be broadly grouped into three major domains, which includes photo-degradation, biological degradation and chemical degradation. The biological route uses fungal/bacterial degradation, but the slow rate of action is the major drawback of this method. This calls for the need to develop a means and a proper channel of steps that would enhance the process. The idea proposed in this project aims at optimizing the process of degradation of plastics and suggests a system that can be used as an alternative of the physical/chemical decomposition of plastics which is in practice at present [3].

In this project, photo-degradation is followed by biological degradation. LDPE needs to be treated before biological degradation, as the fungi treatment is not effective without a pre-treatment of the LDPE sample films. Fungi treatment plays an important role in the biological decomposition of material. However, the high molecular weight, 3-dimensional structure, hydrophobic nature and lack of functional groups in the LDPE interfere with microbial attack [4, 5]. The UV irradiation (photo-oxidation) and thermal and chemical oxidation of PE prior to its exposure to a biotic environment enhances biodegradation. PE polymers are broken down to simpler forms/lower molecular weight polymers which can be easily attacked by biological means. The various chemical, physical and biological changes in the structure of the polymer occurs due to the stresses applied to it, which results in the degradation of the chains into simpler forms. Exposing the polymers to photo-catalyzed UV degradation causes damage to the chemical bonds, which tends to break. Further, growth of fungi on the LDPE surface causes the small-scale deterioration, bursting and swelling of the polymer chains as these fungi penetrate into the solid surface [6]. The combined action of the two means breakdown the higher molecular weight polymers into the forms which can be absorbed by the microbes and biodegraded.

2. MATERIALS AND METHODS

2.1. Chemicals Used

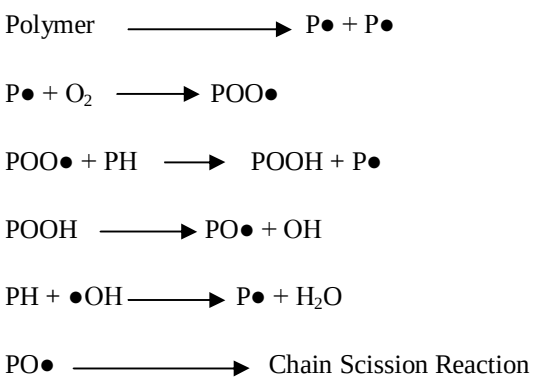
All the chemicals of analytical grade (AR) from Merc and S.D. fine chemicals, India were used in this study. All solutions were prepared as described by Shankar et al., 2016. All the solutions were prepared in distilled water with resistivity of 18.2 MΩ cm (Q-H2O, Millipore Corp.). all the analysis was performed at Department of Applied Sciences and Department of Chemical Engineering of Madan Mohan Malaviya Universityof Technology, Gorakhpur.

2.2. UV Treatment of Polyethylene

Initially, standard sample of polyethylene (PE) mainly LDPE was taken for the UV treatment. The Irradiation with ultraviolet ray source was used to degrade the sample by the process of photo-degradation in the UV chamber in the presence of air. The chains weathered resulting into fragments comprising of reduction in the molecular weight, tensile strength, impact, elongation strength and became more brittle. The reaction initiates with the formation of free radical formed by the photon absorption and fastens if chromophoric groups are present in the polymers.

The generated free radicals react with the atmospheric oxygen to form a peroxy polymer radical. It reacts with the molecules to form polymer hydro-peroxide and a new polymer radical. Polymer hydro-peroxide is further broken into polymer oxy radicals and hydroxy radicals. Some are cross linked to form other molecules while others remain in the form of free radicals. Hence, the polymer is fragmented, the long chains present in the polyethylene which takes a longer time for self-degradation are collapsed into microscopic fragments by UV rays. The sample was treated for 15 days.

Mechanism Involved:



Where, PH = Polymer

P• = Polymer alkyl radical

PO• = Polymer oxy radical (Polymer alkoxy radical)

POO• = Polymer peroxy radical (Polymer alkyl peroxy radical)

POOH = Polymer hydro-peroxide

HO• = Hydroxy radical

2.3. Treatment with TiO_2 and Ascorbic Acid

The whole setup of sample after 15 days of UV treatment was put up in a heating chamber. Constant Temperature around 100℃ was maintained. The sample was heated for 12 hours. TiO_2 was used as a catalyst. Before using it surface modification of TiO_2 was done. 5 g of TiO_2 was added to 50 ml of distilled water. 3 g of ascorbic acid was added to 50 ml of distilled water. The aqueous TiO_2 solution was mixed with the ascorbic acid solution. The whole solution was stirred for 45 minutes to ensure proper mixing. Centrifugation process was done to separate out the precipitate. The precipitate was washed to remove the unmixed Ascorbic acid and TiO_2. The washed sample was heated in an oven at 80℃ for 24 hours.

The 15 days treated sample of PE was mixed with the extracted dried precipitate. A simple composite film was made by a roller mixer at a linear angle. The temperature 150 °C was maintained. Whole sample was treated for 15 minutes. A PE, TiO_2 and ascorbic acid composite film was prepared for the UV treatment. The film was put up under UV source for 45 days. The sample was rotated every day to ensure proper catalyzation.

2.4. Biological treatment

Post photo-degradation, sample was prepared for the biological treatment. *Aspergillus Niger* was used for degrading the PE sample which was treated for the one month.

2.4.1. Isolation of *Aspergillus Niger*

For the preparation of growth medium, 25 g of the mixture of infused potato and dextrose (10:1) was added to 1000 ml distilled water. The mixture was swirled for mixing; heat was applied for complete dissolution. The solution was autoclaved (121°C) for 20 minutes. The solution was cooled before use, and the cap was tightened.

For preparation of potato agar plates, 1L of potato dextrose broth was taken in a flask. 15 g of agar (1.5%) was added to the flask. The solution was mixed by swirling. A piece of aluminum foil was used to cover the top, and it was covered with autoclave tape. Water was added to the mixture and it was autoclaved (121°C) for 15 minutes on Liquid Cycle. After the cycle, it was cooled to ~50°C and antibiotics were added to the mixture. The 20-25mL of the prepared media was poured in 15×100 mm petri dishes, these plates were stored in the cold room. Since, the colonies of the mixed microorganisms were cultured, a dense growth was observed. This sample was then diluted 10^6 times by series dilution. *Aspergillus Niger* was isolated into potato dextrose agar plates from the diluted sample [7].

Isolated sample of *Aspergillus Niger* was cultured in Potato dextrose broth. The sample was left in the medium for two days. The pH of the sample was kept around 5.1 i.e. acidic, in order to decrease bacterial growth. The obtained sample was acclimatized, so as make it favorable for the decomposition of the LDPE sample obtained after the UV photo-catalytic degradation. Acclimatization was done by introducing PE powder to the medium.

2.4.2. Biological treatment with *Aspergillus Niger*

Post photo-degradation, sample was prepared for the biological treatment. The treated sample was cooled and was brought to the room temperature (30-35°C) for optimizing the suitable conditions for fungal treatment. Potato dextrose broth and Potato dextrose agar plate were used for the growth and isolation of *Aspergillus Niger* collected from the dextrose of potato (locally available). The sample was mixed with the *Aspergillus Niger* sample after its acclimatization. The pH was maintained by earlier addition of the ascorbic acid to ensure growth of the fungi in the fragmented medium. Thewhole sample treatment was done for the period of one month

3. RESULTS AND DISCUSSIONS

3.1. Growth Study of *Aspergillus Niger* in NB Media

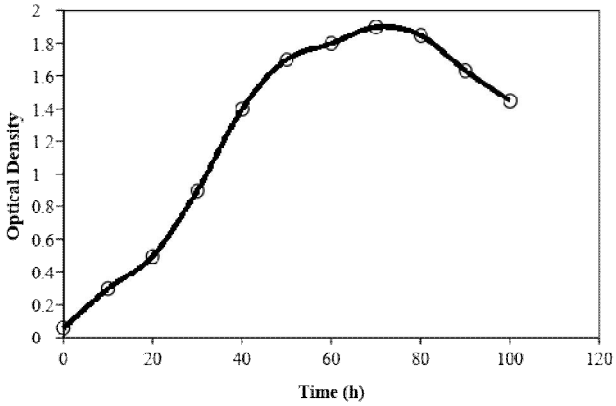


Fig. 1: Growth pattern of microorganisms used in the present investigation (Conditions: Operating temperature: 35°C, pH:5.1)

For the growth study of *Aspergillus Niger* in Nutrient Broth (NB) media, the isolated fungi were selected, and growth of fungi has been studied in nutrient broth media. Thereafter, the acclimatization has been done by gradual decrease in the nutrient concentration by dilution of the NB media with synthetic solution [8].

The optical density (O.D.) of fungal growth culture accumulated in NB medium at a wavelength of 600 nm has been measured at different time intervals and plotted as shown in the Figure 1.

From Figure 1, it is seen that at the initial stage, the O.D. value increases slowly with increase in time up to around 10 h, thereafter it increased very fast within the time period of 10-48 h and remains almost constant up to 70 h. It is an established fact that the carbon source in the media increases the fungi growth. Another observation attributes to the fungal growth pattern, which can be observed to be composed of lag phase (initial 5 h), log phase (5-65 h), stationary phase (65-75 h) and decay phase (> 70 h).

3.2. Effect of Nutrient Concentration on Growth of *Aspergillus Niger*

The effect of nutrient concentration on the growth of *Aspergillus Niger* is shown in Figure 2. From Figure 2, with decrease in nutrient concentration, the final O.D. after 70 h agitation, decreases gradually and reaches minimum value. The above observation can be explained on the fact that the number of fungal cells in the media depends on the carbon source. In the present case with the decrease in the NB broth concentration the carbon source in the solution gradually decreases. From Figure 2, it is evident that O.D. value

decreases from 1.9 to 0.61 with the decrease in nutrient concentration. This can be attributed to the fact that with the decrease of nutrient source in the media, the multiplication of fungal cells decreases, which results in the decrease in O.D. value of the media. It seems that the above fungi can survive under starvation with lower biomass production.

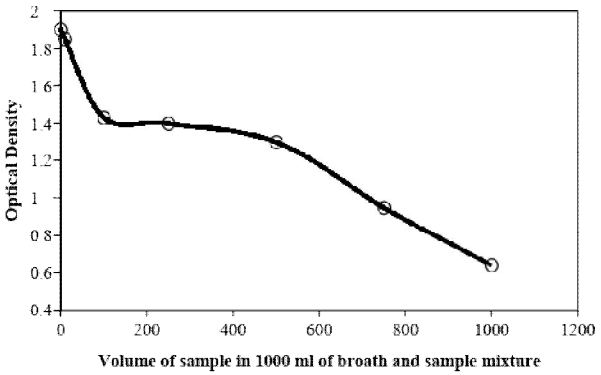


Figure 2.Growth of *Aspergillus Niger* in nutrient deficient environment (Conditions: Operating temperature 35±1°C, pH 7, time 64 h)

3.3. Comparative study

From table 1, biodegradation of different polymers with natural phenomena takes long time but integration of biodegradation of polymers with chemical/physical treatment shortens the time. It is important to note that the rate and extent of polymer consumption can be extensively influenced by abiotic factors that promote oxidation. Biodegradation rate can increase from 0.2% to 8.4% by irradiating the samples with UV light before a biotic treatment [14].

Table 1: Biodegradation of different polymers

Material	Result	Condition	Degradation rate	Reported degradation	Ref
LDPE	Partially biodeg-radable	Bioactive soil	32–37 years in soil	1. About 2/3 decrease of thickness 2. Slow rate of oxidative degradation	[9]
LDPE, LLDPE, HDPE, UHMWPE	Thermally degradable	Addition of metals	Accelerated aging. Thermal degradation caused by contact with metals	1. Decrease in chemilumi-nensence intensity 2. Increase in oxidationrates	[10]
PE	Biodeg-radable	Pre-heated at 60 oC in an air oven to simulate the effect of the compost environment. Incubated in the presence of selected microorganisms	1. Sterilized by UV/ inoculated 30 min] 2. Incubated for 6 months at 27 oC in soil containing 85% of water	1.Microbial growth 2. Erosion of the film surface	[11]
PAH	Biodeg-radable	Buried in extremely acidic environment (coal runoff basin)	28 days	1.60% mineralization 2. CO2 production from 0–10% depending on the hydrocarbon	[12]
LDPE/ starch (12%)	Biodeg-radable	Controlled biologically active soil	7 months	Produced biomass ~300 g/l ~7 g CO2/ 50 ml 17–27% O2 consumption	[13]

4. CONCLUSION

UV treatment and the biological degradation by *Aspergillus Niger*can be seen as an important methodology to overcome the problems arising. The study on the isolation and growth of the fungi using the LDPE as a carbon source it is able to degrade the polyethylene to a greater extent in shorter span of time thereby increasing the efficiency of the process.

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