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Nanoparticles accelerated *in-vitro* biodegradation of LDPE: A review

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ABSTRACT

Plastics are characteristically inert and resistant to microbial attack and therefore they remain in the nature without any deformation for long time. Low Density Polyethylene (LDPE) being an inevitable necessity has spanned high levels of environmental pollution due to its poor waste disposal and thus requires better ways for its degradation management. The conventional methods have shown inadequate degradation with environmental constraints which have been overcome by microbial and enzymatic process of biodegradation. Landfilling, inceration are ways for the disposal of plastic but have number of drawbacks such as lowers water absorption of soil thus reduces the soil fertility. Therefore degradation with the microbes especially by making microbial consortium will be a good choice. Nanoparticles have entered the scientific world with varied potential applications. Studies with nanoparticles have shown their unique ability in enhancement of polymer degradation. Nanoparticles influence the growth profiles of LDPE degrading microorganisms to augment the biodegradation rate, a major problem faced. The review primarily focuses on researches related to the degradation aspect where nanoparticles have acted as enhancers of biodegradation.

Keywords: Biodegradation; Nanoparticles; LDPE; Consortium; FT-IR; TG-DTG-DTA.

INTRODUCTION

The ill effects caused by plastics in the recent years to the environment focused the need for attention and awareness towards plastic degradation. Plastic bags and materials have been used for solid waste collection and disposal from decades. Synthetic plastics, such as polyethylene, are used comprehensively in packaging and other industrial and agricultural applications[**1**]. However, plastic bags and materials can be a disaster for composting systems. Plastics are long hydrocarbon chain, synthetic polymeric molecules and are widely used economical materials which are characterized by excellent all-round properties. They are easy to mold and manufacture. Generally plastics are very stable and not readily degraded. Therefore in today's world environmental pollution from synthetic plastics have been recognized as a major problem. Biodegradable plastics are also of great interest to researchers. Biodegradable plastics are used in many fields like medicine, agriculture, building materials, food packaging industry and toys**[2-5].** In case of biomedical implants and devices, biodegradable plastics are used as implants and can be designed according to the need. There are also plastics which are commercially produced containing additives**[3]**.

This review focuses on biodegradation of LDPE with selected nanoparticles along with microbial consortium. There are varied nanoparticles that enhance growth cycle, mechanical and physiochemical stability along with biodegradability **[6-8].** Nanoparticles are used as nanoclays by forming the nano-composites that have ultra large surface area to volume ratio, also known as clay nano-composites. Using nanoparticles as fillers help in augmenting the material properties along with degradation.**[6]**

Microorganisms for biodegradation

Recently, the biodegradation of plastic waste and the use of microorganisms to degrade the polymers have gained notable importance because of the inefficiency of the chemical and physical disposal methods used for the pollutants, as they causes many environmental hitches. Microorganisms play a substantial role in the biological decomposition of material**.[9].** Fungi have been examined for the biodegradation of LDPE because these organisms produce degrading enzymes**[9]**and, extracellular polymers like as polysaccharides, which can help to colonize the polymer surface**[10]**and the distribution and penetration ability of the fungal hyphae is an advantage.

Studies have investigated the polyethylene biodegradation process using fungal isolates, such as *Phanerochaete chrysosporium***[11],** *Aspergillus niger***[10, 12]**and other strains of the *Aspergillus* genus including *A. terreus, A. fumigates* **[13]** and *A. flavus***[14].**There are reports that bacteria degradepolyethylene**[15]**isolated a biofilm-producing strain of *Rhodococcus ruber* (C208) that degraded PE at a rate of 0.86% per week **[16]**also isolated a thermophilic bacterial strain (707), identified as *Brevibacillus borstelensis*, which utilized standard and photo-oxidized PE..

Two strains of *Aspergillus* sp. and *Lysinibacillus* sp. with remarkable abilities to degrade low-density polyethylene (LDPE) were isolated from landfill soils in Tehran using enrichment culture and screening procedures. UV- and non-UV-irradiated pure LDPE films without pro- oxidant additives in the presence and absence of mixed cultures of selected microorganism was performed for 126 days. The carbon dioxide measurements in the soil showed that the biodegradation in the un-inoculated treatments were slow and were about 7.6% and 8.6% of the mineralization measured for the non-UV-irradiated and UV-irradiated LDPE respectively after 126 days. In contrast, in the presence of the selected microorganisms, biodegradation was much more efficient and the percentages of biodegradation were 29.5% and 15.8% for the UV-irradiated and non-UV-irradiated films, respectively. The percentage decrease in the carbonyl index was higher for the UV-irradiated LDPE when the biodegradation was performed in soil inoculated with the selected microorganisms. These study showed mixed culture help in degradation process**[1].**

Biodegradation of a polymeric material is chemical degradation brought by the action of naturally occurring microorganisms such as bacteria and fungi via enzymatic action into metabolic products of microorganisms (e.g., H2O, CO2, CH4, biomass etc.)**[17-19]**.In contrast to the biodegradation of polymers, where a complete conversion of the material components takes place only a change in the polymer structure or the plastic composition is observed in many cases in polymer bio deterioration or bio corrosion**[20]**. The ultimate result in both the cases are a complete loss of structural integrity as a result of drastic decrease in molecular weight. In current times the term 'biodegradable' is considered an essential property of many manufactured materials to ensure that the particular material with stand its effect or not. Although biodegradation may be seen as a direct opposite to bio deterioration, they are usually the same processes, changed in meaning and significance solely by human need. Hence, in this review the term biodegradation also implicitly include bio corrosion or bio deterioration or microbially influenced corrosion (MIC). Microorganisms are involved in the degradation and deterioration of both synthetic and natural polymers forming biofilms**[20]**. Polymers which are susceptible to biofilm formation include paints, adhesives, plastics, sealants, composites, lubricating materials, fuels etc**[21-23]**.

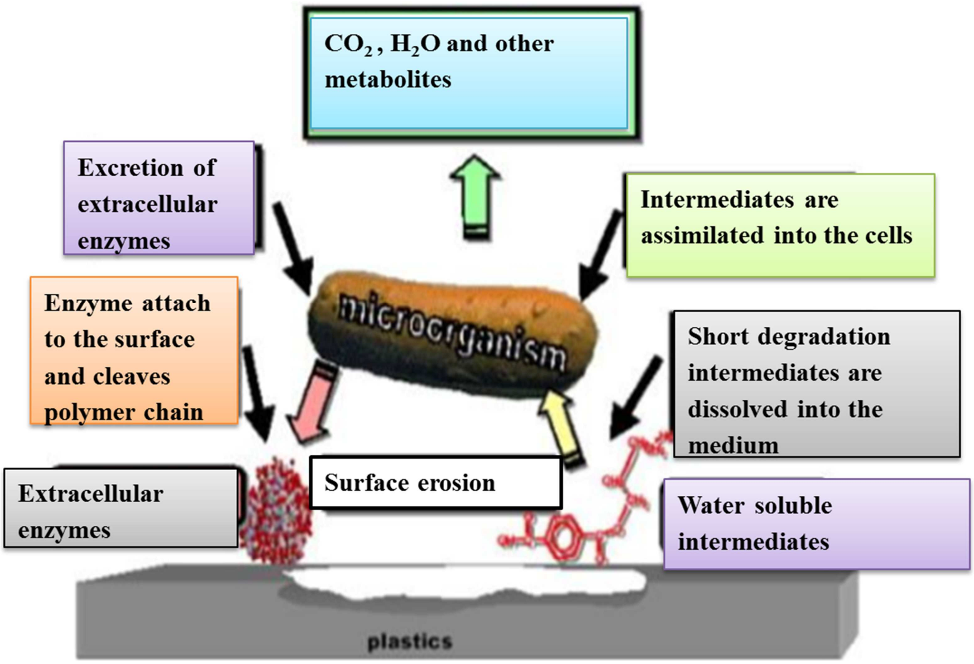
Mode of biodegradation

The biological environment includes the biological agents such as bacteria, fungi and their enzymes responsible for the deterioration of polymeric substances. They consume a substance as a food source so that its original form disappears.

Polymeric materials are potential source of carbon and energy for heterotrophic microorganisms including bacteria and fungi in several ways. The actions of microorganisms on polymers are influenced by two different processes:

1. Direct action: The deterioration of plastics which serve as a nutritive substance for the growth of the microorganisms
2. Indirect action: The influence of metabolic products of the microorganisms, e.g., discoloration or further deterioration**[24].**

Deterioration of polymeric materials is caused by adhering microorganisms that colonize their surfaces, forming biofilm**[25, 26].**



(Modified from Muller 2003)
Fig: 1Mechanism of plastic biodegradation under aerobic conditions

Different microorganisms reported to degrade different types of plastics:

Polyethylene	Polyurethane	Polyvinyl chloride
*Brevibacillus borstelensis***[16]**	*Comamonas acidovoransTB-35***[27]**	*Pseudomonas putida AJ***[28]**
*Rhodococcus rubber***[15, 29]**	*Curvularia senegalensis* **[30]**	*Ochrobactrum TD, Pseudomonas fluorescens***[31]**
*Penicillium simplicissimum***[32]**	*Fusarium solani, Aureobasidium pullulans, Cladosporium sp.***[9]**	*Aspergillus niger, van Tieghem F-1119***[9]**
	Pseudomonas chlororaphis **[33]**	

Nanoparticles as enchancer for biodegradation

Super paramagnetic iron oxide nanoparticles (SPION)

Super paramagnetic iron oxide nanoparticles (SPION) with size ranging 10.6-37.8 nm were synthesized and characterized through XRD, FT-IR spectra, simultaneous TG-DTG-DTA, vibrational sample magnetometry (VSM) and transmission electron microscopy (TEM). Nanoparticle has been synthesized by co-precipitation method with ammonia using ferrous chloride and ferric chloride solutions. Effect of SPION size variants on the growth profile of Low-Density Polyethylene (LDPE) degrading microbial consortium consisting of *Microbacteriumsp., Pseudomonas putida* and *Bacterium Te68R* was monitored in Minimal broth Davis medium lacking iron and dextrose. These nanoparticles improve the exponential phase durability by 36 h thus accelerating the bacterial growth. Further, shifting in lag-phase and the additive effect of sonication was also documented on growth profiling. SPION of size 10.6 nm were found to significantly increase the biodegradation efficiency of consortium as revealed by λ-max shifts, Fourier transform infrared spectroscopy (FT-IR) and simultaneous thermogravimetric-differential thermogravimetry-differential thermal analysis (TG-DTG-DTA). It highlights the significance of bacteria-nanoparticle interactions which can dramatically influence key metabolic processes like biodegradation**[34].**Super magnetic Iron Oxide Nanoparticles (SPION) have been studied in the similar way as that of NBT and Fullerene 60 nanoparticle **[35].**

Nano barium titanate (NBT)
To influence the growth cycle of LDPE degrading bacterial consortia NBT is supplemented in minimal broth. It influences lag phase, exponential phase and stationary phase and acts by reducing the duration of lag phase and increasing the duration of exponential and stationary phase. For the accelerated growth of bacterial consortia NBT is a supportive nutritional component and thus assist the consortia in plastic waste biodegradation. The preferred particle size is 38nm with bacterial consortia of *Microbacterium species strain MK3*, *Pseudomonas putida strain MK4 and Bacterium Te68R strain PN12*[36]**.**Experiment performed with both positive and negative control with and without nanoparticles, where, nanoparticles are sonicated at 50-60 Hz for 2.5 minutes with 0.3 second cycles. UV spectrophotometer is used for monitoring bacterial growth cycle. Consortia is removed from the LDPE by centrifugation and then evaporated to remove water. The residue is analyzed and characterized using FTIR and TG-DTG-DTA where LDPE is taken as control. As the polymeric structure changes, a shift in λmax is observed from 209-225.3 nm. This shift takes 4 days in the absence of NBT. In the presence of NBT, the spectrum shifts from 209-224.11 nm in 2 days, showing an improved degradation action**[35].**

Fullerene 60 Nanoparticles
The Fullerene 60 nanoparticles**[37]**also influence the growth cycle of LDPE degrading bacterial consortia when used in minimal broth Davis without dextrose. Fullerene-60 nanoparticles were used for studying their effect on the low-density polyethylene (LDPE) biodegradation efficiency of two potential polymer-degrading consortia. A total of six bacterial cultures *Microbacterium* sp. strain MK3 (DQ318884), *Pseudomonas putida* strain MK4 (DQ318885), *Bacterium* Te68R strain PN12 (DQ423487). *P. aeruginosa* strain PS1 (EU741797), *P. putida* strain PW1 (EU741798), and *P.aeruginosa* strain C1 (EU753182) were selected for consortium preparation. Consortium 1 comprising MK3, MK4, and PN12 strains, and Consortium 2 comprising PS1, PW1, and C1 strains**[8, 38].** Consortium 1 and 2 both show no affect no growth cycle but there is difference in the degradation pattern, consortium 1 showed more degradation then consortium 2**[37].**

Fullerene-60 used at 0.01% (w/v) concentration due to the fact that they are detrimental to bacterial growth at higher concentrations like 0.25, 0.5, 1%... etc. LDPE used with Fullerene 60 at a concentration of 5 mg/ml **[34]**have worked with these nanoparticles on two different consortia**[35]**. The bacterial strains isolated from degrading polyethylene have capability of degrading HDPE, epoxy and epoxy silicon blends**[39, 40].** The bacteria growth curve analysis using UV Spectrophotometer is done to know the effect of fullerene 60 on individual strains and on consortia. The degraded product is obtained after the consortia has reached stationary phase in case of sonicated nanoparticles .The degraded product obtained after centrifugation and evaporation is analyzed and characterized using FTIR and TG-DTG-DTA where LDPE is taken as control. The polymeric structure changes making a shift in λmax is observed from 209 nm, constant for 2 days, to 220 nm, after 3 days and to 223 nm after 4 days, in absence of Fullerene 60 nanoparticles. Whereas, in the samples with fullerene-60 λmax was found to shift from 209-224.97 nm on 1st day itself, showing an improved rate of degradation. This is the first report whereby fullerene-60, which is otherwise considered toxic, has helped to accelerate the polymer biodegradation process of bacterial consortia**[35].**

CONCLUSION

LDPE degradation has become a serious issue to be deal with because its accumulation is increasing day by day. Many ways of degradation was performed but was effective in certain ways only. Firstly done with single microbial strain then with consortium thus slightly increasing the efficiency of degradation but it’s not up to mark since problem of accumulation is increasing frequently and the solution present can’t withstand it. Therefore the researchers have found nanoparticles as enhancers of microbial degradation ability. Nano barium Titanate (NBT), Fullerene 60 and Super magnetic iron oxide (SPION) have been reported to degrade LDPE with the help microbial activity enhancement. Nanoparticles, being a new field in the advancement of study related to biodegradation since it deals with the growth profiling of microbe**.**

Therefore this field has got potential to be explored with other documented nanoparticles like Cobalt ferrite and other silica based nanoparticles that influence the bacterial growth profiles. Till now no work has been done with fungal consortium along with nanoparticles therefore this can also be explore because rate of degradation with fungus is more since it is cited in literature.

The degradation mechanisms are also not known in much detail and consequently open a new direction for biodegradation related studies. Therefore, the implications of nanoparticles have got wide applications as biodegradation enhancers of synthetic plastics.

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