Degradation, Detection and Separation of Polyethylene Terephthalate Waste at Different Size Ranges

A thesis submitted towards partial fulfillment of the requirement for the degree of Master of Technology in Nano Science and Technology

Submitted by :

Kamalesh Roy
Roll No. : M4NST22019
Class Roll No. : 002030701020
Registration No. : 154588 of 2020-2021

Under the Guidance of :

Dr. Chandan Kumar Ghosh
School of Material Science and Nanotechnology
Jadavpur University
Kolkata - 700032

Course Affiliated to :
Faculty of Interdisciplinary Studies, Law and Management
Jadavpur University
Kolkata - 700032

2022

CERTIFICATE OF RECOMMENDATION

This is to certify that the thesis entitled "**Degradation, Detection and Separation of Polyethylene Terephthalate Waste at Different Size Ranges**" has been carried out by **Kamalesh Roy** in the fulfillment of the requirements for the degree of the **Master of Technology in Nano Science and Technology** from **Jadavpur University, Kolkata** is recorded as bona fide work that has been conducted under the supervision of **Dr. Chandan Kumar Ghosh**. The contents embodied in the thesis have not been submitted to any other university for the award of any degree or diploma.

Dr. Chandan Kumar Ghosh
Thesis Supervisor
School of Material Science and Nanotechnology
Jadavpur University
Kolkata-32

Prof. (Dr.) Sourav Sarkar
Director
School of Material Science and Nanotechnology
Jadavpur university
Kolkata-32

Dean of Faculty of Interdisciplinary Studies, Law and Management
Jadavpur University
Kolkata-32

Declaration of Originality and Compliance of Academic Ethics

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his Master of Technology in Nano Science and Technology program during the academic year 2020 -2022. All information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Kamalesh Roy
Exam Roll No. : M4NST22019
Class Roll No. : 002030701020
Registration No. : 154588 of 2020-2021

CERTIFICATE OF APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject and presented in a manner satisfactory to warrant acceptance as prerequisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not necessarily endorse or approve any statement made, opinion expressed or conclusion drawn therein, but approve the thesis only for which it is submitted.

Committee of the final Examination

Signature of the
Examiner

Signature of the
Supervisor

To,
Runnu Horo!
To The Struggle!

To Maa and Baba
To My beloved Natunpara, River Teesta

Acknowledgement

I am very grateful to everyone who has been a part of this beautiful journey!

Table of Contents

Abstract

This thesis titled “Degradation, Detection and Separation of Polyethylene Terephthalate Waste at Different Size Ranges” primarily concerned with two topics : firstly, degradation of Polyethylene Terephthalate (PET) at mild condition via various alkaline hydrolysis processes and secondly, investigates the characteristics of Micro and Nano sized plastics; an effort to study their detection and separation have been also made.

Introduction

Historically, the realization of every legendary technological feat that human civilization has achieved since prehistoric times owe much to the right choice of material that possesses the potential to transform the abstraction of science to a tangible triumph of man over nature. No stone age man would have been capable of harnessing fire without the right sparking rocks. There would be no Indus Valley civilization with its large cities and millions of people without the best quality of Bronze. Probably, the entire Ganges Civilisation would have remained dense thick forest without the wootz steel that was tempered in India in mid-1st millennium BC.

Leo Baekeland revolutionized the imagination of material when he invented Bakelite in 1907. Bakelite was the first synthetic polymer or plastic. Then in 1912 Victor Regnault invented PVC. Then in the next four decades the world saw seven major synthetic polymers (cellophane, PMMA, Polyethylene, Polyurethane, Nylon, Polystyrene and Polypropylene). [1] It was so fascinating and wonderful array of inventions that the French Philosopher Ronald Barthes writing in 1950 :

> *"So, more than a substance, plastic is the very idea of its infinite transformation; ..It is ubiquity made visible...Plastic is, all told, a spectacle to be deciphered... the very spectacle of its end-products...The reverie of man at the sight of the proliferating forms of matter, and the connections he detects between the singular of the origin and the plural of the effects."*

Synthetic polymers were considered as an enigma at its birthbed. It was adored as one of the bestest feats human civilization has ever achieved by inventing plastics. In the next two decades, plastic production increased around twenty fold and within the next half a century it has become so available, so innate and so inherent in our everyday life that 12 million ton of plastic waste is poured into our oceans every year. It has become so omnipresent that an estimated 5 trillion plastic debris are floating on the sea. [2]. The extent of plastic ubiquity is so powerful that it constantly changes the shape and size and permeates every sphere of the ecosystem. Plastic debris transforms into macro and eventually micro and nano sized particles having its manueverlity from our coastline to farthest nook of the arctic sphere [3]. The limitless ubiquity of plastic particles has made its footprint even in our bloodstream [4]. Microplastics have started changing our soil and affecting the cropping pattern of plants probably since decades [5]. It has recently been studied that fruits and vegetable samples are loaded with thousands of microplastic particles (from 50k to 200k particles per gram) [6]. Today, the delicate polypropylene feeding bottles are actually facilitating microplastic uptake in infants [7]. As per the study, average microplastic uptake is 1.5 million particles per infant per day. Microplastics we consume with our extremely plasticized lifestyle are changing the behavior of our gut microorganisms too [8]. The tiniest plastic particles that are the direct product of global plastic debris as a result of constant chemical and mechanical stresses under natural conditions have started invading the entire aquatic ecosystem from the very bottom of the food chain [9]. Fish as well as fishmeal is contaminated with micro fiber of different plastics [10]. It does not even spare the fishes from its very embryonic stages [11]. As we know, Corals are bleaching all over the world these days. Micro and nano plastics are adding their part too! Some of them are replacing zooxanthellae impacting coral-symbiont coexistence while some others are directly bleaching reefs [12].

Plastics, from its days of reckoning as a spectacle of wonder has become a specter that is haunting every facades of our life and ecosystem. Current research on micro and nanoplastics are at its infancy. In most of the cases, we lack in-depth study regarding their toxicity and related hazardous effects. Scientific community is not in consensus on many questions related to the tiny debris of synthetic polymers. There are thousands of other answers that need to be searched out. There is an entire horizon that is left untrodden when it comes to detect, separate and degrade the Frankenstein we have created not long ago!

The total amount of virgin plastics produced to this point is thought to be 8300 million metric tonnes (Mt). Approximately 6300 Mt of plastic garbage has been produced as of 2015; just 9% of this material was recycled, 12% was burned, and 79% was left to pile in landfills or the environment. By 2050, 12,000 Mt of plastic garbage will be in landfills or the environment, depending on how waste is managed and produced now [13]. Polymers degrade mechanically during recycling to the point that they become useless after a few cycles. The embedded chemical feedstocks can also be recovered for use in new industrial processes by chemical recycling to monomers. The techniques are still resource-intensive and can only be used to chemically recycle a small subset of total commodity polymers produced [14]. The

PET, HDPE, polystyrene (PS), and nylon-6 waste can be chemically broken down and converted back into monomer, which is not only a popular option but also a promising one. Chemical depolymerization methods such as pyrolysis, catalysis, or enzymatic processes, as well as the chemical separations required to convert the waste plastic feedstocks for reuse, are extremely energy intensive and have a higher carbon footprint [14].

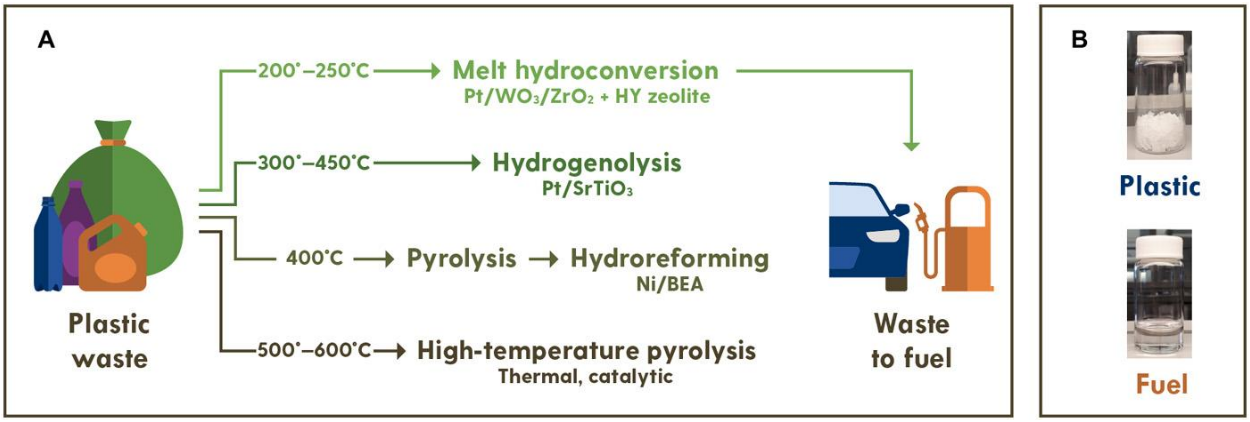
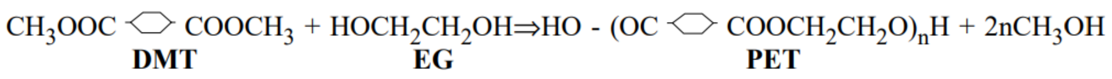


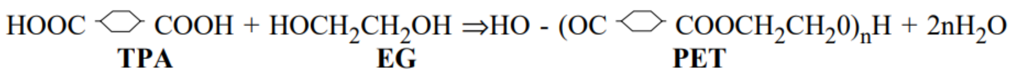
Fig. : Fig. 1 Current and proposed chemical conversion of plastic-waste to fuels. (A) Polyolefin pyrolysis and hydrogenolysis require harsh reaction conditions and produce low amounts of fuel-range hydrocarbons. The proposed approach exhibits a high yield to gasoline at low temperatures without solvents or diluents. (B) Initial chopped PE bag before reaction and liquid product after reaction. Photo credit: Pavel Kots, University of Delaware. Source : https://www.science.org/doi/10.1126/sciadv.abf8283

In case of Polyethylene Terephthalate (PET), like all other popular synthetic plastics, the degradation processes converting the waste to its precursors, have high temperature and high pressure demands in order to achieve industrial efficiency [15]. At the same time since the US Shale Boom of 2008, the relevance of PET waste recycling has become questionable, in particular. To understand the current uncertainty that is looming large in the PET recycling industry, one must look at the precursors of PET. Primary precursors for PET are Terephthalic Acid (TPA) and Ethylene Glycol (EG). In the manufacturing of PET resins, ethylene glycol (EG) and either dimethyl terephthalate (DMT) or terephthalic acid are used (TPA). Solids include TPA and DMT. TPA sublimes, while DMT has a melting point of 140°C (284°F). The intermediate bis-(2-hydroxyethyl)-terephthalate (BHET) monomer and either methanol (DMT process) or water are initially produced by both procedures (TPA process). The BHET monomer is then polymerized with heat, a catalyst, and decreased pressure to create PET resins. The following is the main response to the DMT process:

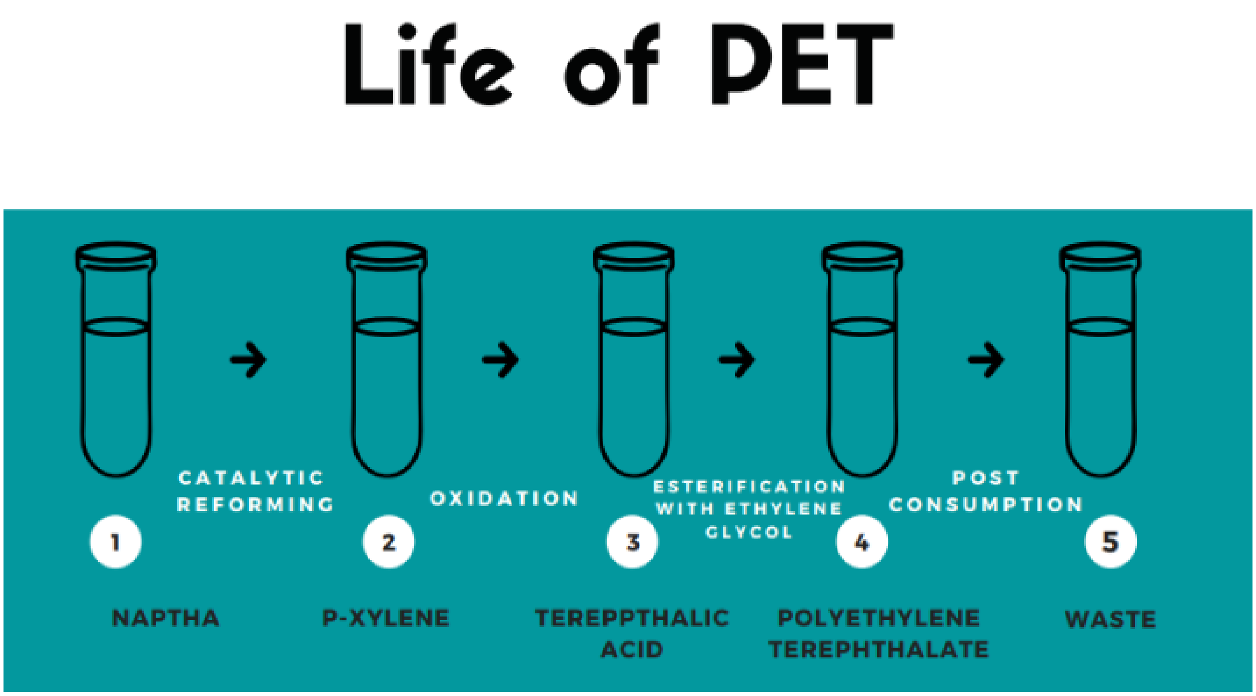


$$\underset{\textbf{DMT}}{CH_3OOC \bigcirc COOCH_3} + \underset{\textbf{EG}}{HOCH_2CH_2OH} \Rightarrow \underset{\textbf{PET}}{HO - (OC \bigcirc COOCH_2CH_2O)_nH} + 2nCH_3OH$$

The primary reaction for the TPA process is:



$$\underset{\textbf{TPA}}{HOOC \bigcirc COOH} + \underset{\textbf{EG}}{HOCH_2CH_2OH} \Rightarrow \underset{\textbf{PET}}{HO - (OC \bigcirc COOCH_2CH_20)_nH} + 2nH_2O$$



TPA is a direct product of p-xylene oxidation and p-xylene industrially is sourced from the catalytic reforming of Naphtha. Studies revealed that the US shale boom-induced decreasing trend in ethane prices increased propylene prices while lowering ethylene costs. While naphtha has lost its ability to anticipate both, propane still acts as a predictor of the latter. The comparison statistics showed that although Japan relies on crude oil and refined naphtha, the US manufactures the majority of its petrochemical products from natural gas based feedstocks [16]. As of June, the average OPEC oil price for the coming year is 105.06 dollars per barrel.

This is an increase from 69.72 dollars the previous year and follows sanctions on Russia as a result of the Russia-Ukraine war and a shortfall in energy supplies.

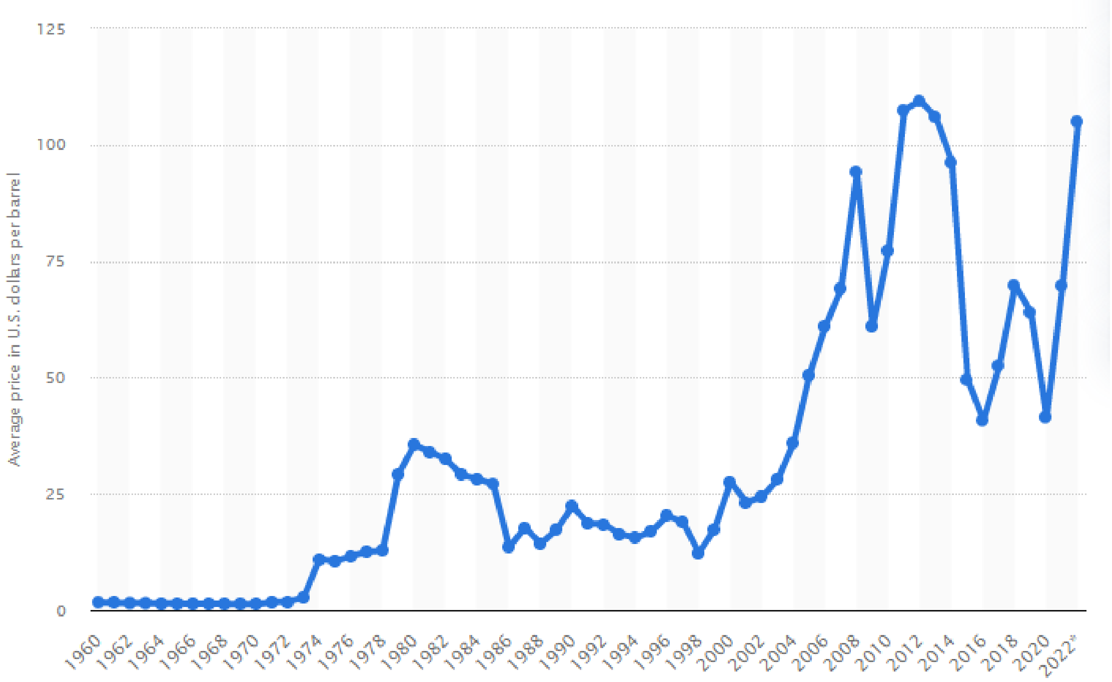


Fig. Per Barrel crude oil price increase in the Period 1960-2022

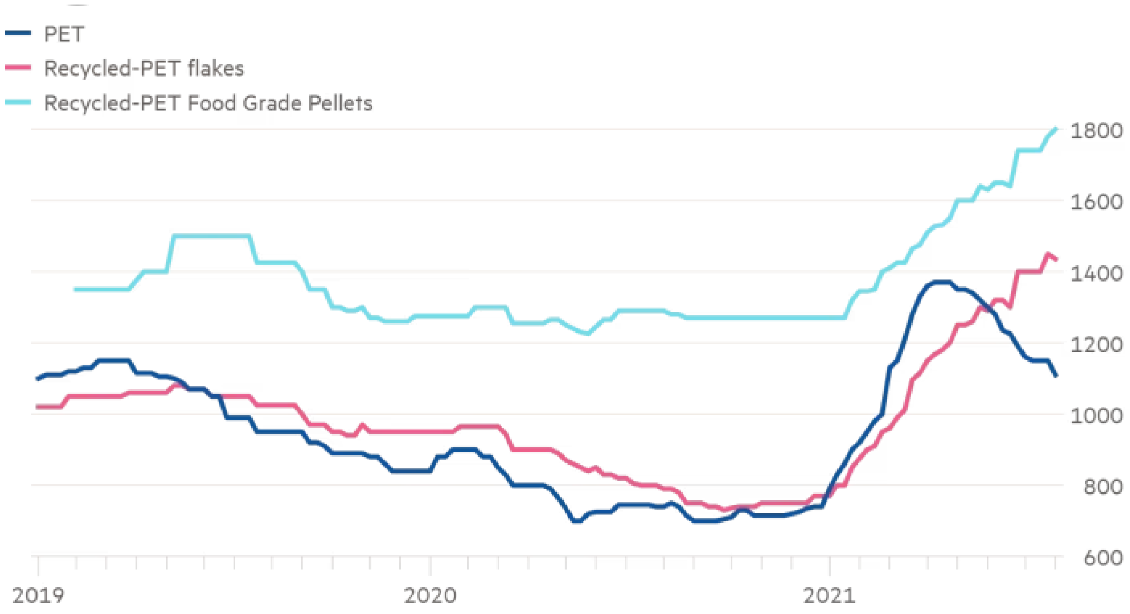


Fig. Change in the prices of PET, Recycled-PET Flakes and Recycled-PET Food Grade Pellets.

Source : S&P global Platts

https://www.spglobal.com/commodityinsights/en/about-commodityinsights/media-center/press-releases/2020/11162020-new-recycled-pet-assessments

Recycled PET, or rPET, costs €1,050 per tonne as of 2019, which is around €200 less than virgin PET. The cost has now increased to €1,435. Food grade rPET, which is more costly and frequently transparent and is used to package consumer items, costs €1,800 a tonne. So, due to the fluctuation in the price of PET precursors and for various unavoidable technological as well as economic circumstances in the field of PET recycling industry, the possibilities of waste to PET route is full of difficulties and financial uncertainty. And last but not the least the sheer amount of energy and resource requirement as well as environmentally carbon heavy pathways of PET recycling demands nothing but a paradigm shift from the perspective of technology, economy and policymakers. The need for processes that are mild in reaction condition, minimalistic in resource requirement and have potential to produce valuable products other than the plastic precursors are utmost needed to deal with the millions of tons of PET plastics that has become so ubiquitous in our real life.

Plastic is the omnipresent material in our 21st century lifestyle and so are the ubiquitous presence of microplastics all over nature [17]. Although the earliest reports on macro plastic pollution were in late 70s [18] [19], it was Plymouth University Marine Biologist Richard Thompsons who first reported that the size of mega and macro-plastic debris in the oceans are decreasing and concluded that the fate of human made billions of tons of plastic debris and their natural fragmentation into tiniest smaller micro-plastics must be studied to appraise their ecological consequences [20]. Since the seminal report by Richard Thompson, in the next one and half decade research on microplastics have grown exponentially; Bibliographic statistics implies that around 2501 papers have been published till 2020 [21]. Apart from Macro sized PET plastics, the continuous chains scission and size reduction due to different environmental factors, the ubiquity of plastics become more complex and hence further irreversible. Therefore, to imagine the world of waste is not only confined within the perimeter of the largest landfill in any city but the constant change in size, and hence surface activity, sorption properties etc have made the problems of plastics multilayered. Current research provides much evidence of their bioaccumulation and their penetration to the bottom of our food chain. To mitigate such problems needs the identification of the problem in quantity as well as in quality, to be specific.

As we already know, human civilization has already produced more than 6300 million tonnes of plastic since 1950 [22]. Global scientific community poses no disagreement regarding the omnipresence of microplastics [23]. In spite of reaching a solid consensus regarding the abundance, uptake and transport of microplastics from the consumer end to environmental accumulation at different levels of the food chain and ecology [17], [24]- [27], the current knowledge on microplastic is yet to achieve the paradigm shift towards formulating the scientific consistency [28] [29] regarding the detailed environmental fate of microplastics [30] [31], their stability and behavior in natural colloidal systems , their capacity and heterogeneity of agglomeration at different pH, their interactions with other pollutants and hydrophobic Organic Chemicals [32] - [37].

During the last one decade, the majority of the studies on micro and nano plastics are on laboratory scale, involve very few polymer types [frequent studies on polystyrene while polystyrene contributes to only 6% of global plastic waste] and most of the microplastics are commercially sourced [Instead of naturally weathered] [28][32].

It is undoubtedly evident that consideration of natural environment like parameters brings about newer insights regarding microplastics [38]. Studies show that the combined effect of microplastics is different than the fresh one [39]. Uptake of different pollutants in aquatic life intensifies in presence of microplastics [40].

There has been more research on the sorption behavior of microplastics in recent years [41] [42]. Different chemical pollutants, pharmaceuticals, and various natural organic matter shows strong affinity towards microplastics [43] [44].

Therefore , it is evident that while designing realistic detection, separation and degradation protocols for microplastics in aqueous environments, we must consider the complex effects of various natural parameters. The combination of laboratory studies and the field verification of the same can complement each other in the development of better detection and separation protocols.

Within the scope of this thesis, I have considered PET plastics only. For degradation of PET, studies at milder conditions (30 °C - 70 °C) have been carried out. Also, a nanocatalyst was synthesized for faster degradation of PET with a reaction design which is environmentally sustainable and materials used are recyclable. In the last chapter, synthesis of micro and nano sized PET plastic at laboratory scale have been carried out. Accumulation of nanoplastics in Brine Shrimp as well as their penetration in cellular environments have been studied. A Layered Double Hydroxide (LDH) - Polysulfone (PSF) membrane was also fabricated for the purpose of waste micro and nano PET plastic removal.

References

[1] Chalmin, Philippe. "The history of plastics: from the Capitol to Tarpeian Rock." Field actions science reports. The Journal of Field Actions Special Issue 19 (2019): 6-11.

[2] Eriksen, Marcus, et al. "Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea." PloS one 9.12 (2014): e111913.

[3] Peeken, Ilka, et al. "Arctic sea ice is an important temporal sink and means of transport for microplastic." *Nature communications* 9.1 (2018): 1-12.

[4] Leslie, Heather A., et al. "Discovery and quantification of plastic particle pollution in human blood." *Environment International* 163 (2022): 107199.

[5] de Souza Machado, Anderson Abel, et al. "Microplastics can change soil properties and affect plant performance." *Environmental science & technology* 53.10 (2019): 6044-6052.

[6] Conti, Gea Oliveri, et al. "Micro-and nano-plastics in edible fruit and vegetables. The first diet risks assessment for the general population." *Environmental Research* 187 (2020): 109677.

[7] Li, Dunzhu, et al. "Microplastic release from the degradation of polypropylene feeding bottles during infant formula preparation." *Nature food* 1.11 (2020): 746-754.

[8] Tamargo, Alba, et al. "PET microplastics affect human gut microbiota communities during simulated gastrointestinal digestion, first evidence of plausible polymer biodegradation during

human digestion." *Scientific reports* 12.1 (2022): 1-15.

[9] Suman, Thodhal Yoganandham, et al. "Acute and chronic effects of polystyrene microplastics on brine shrimp: First evidence highlighting the molecular mechanism through transcriptome analysis." *Journal of hazardous materials* 400 (2020): 123220.

[10] Thiele, Christina J., et al. "Microplastics in fish and fishmeal: an emerging environmental challenge?." *Scientific reports* 11.1 (2021): 1-12.

[11] Bhagat, Jacky, et al. "Zebrafish: An emerging model to study microplastic and nanoplastic toxicity." *Science of The Total Environment* 728 (2020): 138707.

[12] Huang, Wei, et al. "Microplastics in the coral reefs and their potential impacts on corals: A mini-review." *Science of The Total Environment* 762 (2021): 143112.

[13] Geyer, Roland, Jenna R. Jambeck, and Kara Lavender Law. "Production, use, and fate of all plastics ever made." *Science advances* 3.7 (2017): e1700782.

[14] Vora, Nemi, et al. "Leveling the cost and carbon footprint of circular polymers that are chemically recycled to monomer." *Science advances* 7.15 (2021): eabf0187.

[15] Ügdüler, Sibel, et al. "Towards closed-loop recycling of multilayer and coloured PET plastic waste by alkaline hydrolysis." *Green chemistry* 22.16 (2020): 5376-5394.

[16] Kim, Soohyeon, Saerok Jeong, and Eunyoung Heo. "Effects of the shale boom on ethylene and propylene prices." *Energy Sources, Part B: Economics, Planning, and Policy* 14.3 (2019): 49-66.

[17] Barnes, David KA, et al. "Accumulation and fragmentation of plastic debris in global environments." Philosophical transactions of the royal society B: biological sciences 364.1526 (2009): 1985-1998.

[18] Parslow, J. L. F., and D. J. Jefferies. "Elastic thread pollution of puffins." *Marine Pollution Bulletin* 3.3 (1972): 43-45.

[19] Kenyon, Karl W., and Eugene Kridler. "Laysan albatrosses swallow indigestible matter." *The Auk* 86.2 (1969): 339-343.

[20] Thompson, Richard C., et al. "Lost at sea: where is all the plastic?." *Science* 304.5672 (2004): 838-838.

[21] Zhang, Ying, et al. "Global trends and prospects in microplastics research: A bibliometric analysis." *Journal of Hazardous Materials* 400 (2020): 123110.

[22] Chinthapalli, Raj, et al. "Biobased building blocks and polymers—global capacities, production and trends, 2018–2023." *Industrial Biotechnology* 15.4 (2019): 237-241.

[23] Lim, XiaoZhi. "Microplastics are everywhere—but are they harmful?." (2021): 22-25.

[24] Napper, Imogen Ellen, and Richard C. Thompson. "Plastic debris in the marine environment: history and future challenges." *Global Challenges* 4.6 (2020): 1900081.

[25] MacLeod, Matthew, et al. "The global threat from plastic pollution." *Science* 373.6550 (2021): 61-65.

[26] Rillig, Matthias C., and Anika Lehmann. "Microplastic in terrestrial ecosystems." *Science* 368.6498 (2020): 1430-1431.

[27] Mitrano, Denise M., Peter Wick, and Bernd Nowack. "Placing nanoplastics in the context of global plastic pollution." *Nature nanotechnology* 16.5 (2021): 491-500.

[28] Hartmann, N. B. "Hü ffer T, Thompson RC, Hassellö v M, Verschoor A, Daugaard AE, et al. Are We Speaking the Same Language? Recommendations for a Definition and Categorization Framework for Plastic Debris." *Environ Sci Technol* 53.3 (2019): 1039-47.

[29] Wang, Liuwei, et al. "Environmental fate, toxicity and risk management strategies of nanoplastics in the environment: Current status and future perspectives." *Journal of hazardous materials* 401 (2021): 123415.
[30] MacLeod, Matthew, et al. "The global threat from plastic pollution." *Science* 373.6550 (2021): 61-65.
[31] Waldman, Walter R., and Matthias C. Rillig. "Microplastic research should embrace the complexity of secondary particles." (2020): 7751-7753.
[32] Shen, Maocai, et al. "Recent advances in toxicological research of nanoplastics in the environment: A review." *Environmental pollution* 252 (2019): 511-521.

[33] Koelmans, Albert A., et al. "Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies."

Environmental science & technology 50.7 (2016): 3315-3326.

[34] Sander, Michael, Hans-Peter E. Kohler, and Kristopher McNeill. "Assessing the environmental transformation of nanoplastic through 13C-labeled polymers." *Nature Nanotechnology* 14.4 (2019): 301-303.

[35] Oliveira, M., and M. Almeida. "The why and how of micro (nano) plastic research." *TrAC Trends in analytical chemistry* 114 (2019): 196-201.

[36] Sun, Hongyan, Ruyuan Jiao, and Dongsheng Wang. "The difference of aggregation mechanism between microplastics and nanoplastics: Role of Brownian motion and structural layer force." *Environmental Pollution* 268 (2021): 115942.

[37] Sharma, Virender K., et al. "Environmental factors-mediated behavior of microplastics and nanoplastics in water: A review." *Chemosphere* 271 (2021): 129597.

[38] Mato, Yukie, et al. "Plastic resin pellets as a transport medium for toxic chemicals in the marine environment." *Environmental science & technology* 35.2 (2001): 318-324.

[39] Dong, Shuangshuang, et al. ``Combinational effect of titanium dioxide nanoparticles and nano polystyrene particles at environmentally relevant concentrations on nematode Caenorhabditis elegans." *Ecotoxicology and environmental safety* 161 (2018): 444-450.

[40] Chen, Qiqing, et al. "Enhanced uptake of BPA in the presence of nanoplastics can lead to neurotoxic effects in adult zebrafish." *Science of the Total Environment* 609 (2017): 1312-1321.

[41] Munoz, Macarena, et al. "Adsorption of micropollutants onto realistic microplastics: Role of microplastic nature, size, age, and NOM fouling." *Chemosphere* 283 (2021): 131085.

[42] Naqash, Nafiaah, et al. "Interaction of freshwater microplastics with biota and heavy metals: a review." *Environmental Chemistry Letters* 18.6 (2020): 1813-1824.

[43] Fred-Ahmadu, Omowunmi H., et al. "Interaction of chemical contaminants with microplastics: principles and perspectives." *Science of the Total Environment* 706 (2020): 135978.

[44] Puckowski, Alan, et al. "Sorption of pharmaceuticals on the surface of microplastics." *Chemosphere* 263 (2021): 127976.

Literature Review

On Macro sized PET Degradation :

PET is a thermoplastic polyester that is semi-crystalline and has the qualities of high strength, transparency, and safety. The intermediates, pure terephthalic acid (TPA) and ethylene glycol (EG), used in the production of PET, are produced from crude oil. The initial result of heating the two components is a mixture of low molecular weight polymers and the monomer bis(2-hydroxyethyl) terephthalate (BHET) (oligomers). As the mixture continues to react, further ethylene glycol is separated, and the PET is created. The PET is a viscous molten liquid at this point. To create an amorphous material that resembles glass, it is extruded and water quenched. Additionally, some PET is produced via a technique based on terephthalic acid's dimethyl ester (DMT) [1].

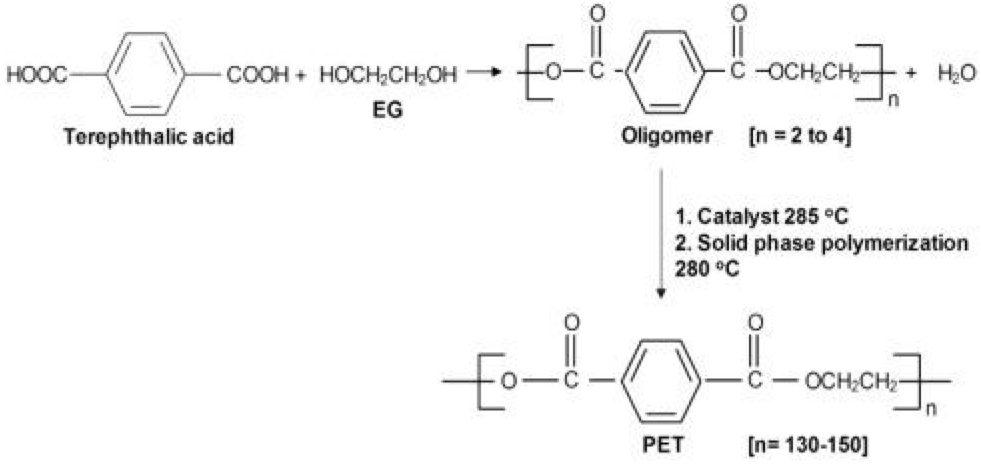


Fig. PET Production Chemical Reaction. Source [2]

The worldwide PET market is now dominated by two kinds of PET: bottle-grade PET and fiber-grade PET. These standard grades differ primarily in optical appearance, production methods, and intrinsic viscosity (IV), or molecular weight, if appropriate. The latter are distinguished by the quantity and kind of co-monomers, stabilizers, metal catalysts, and colorants. PET that is suitable for use in textile fibers has a molecular weight of 15,000–20,000 g/mol, translating to an inherent viscosity of 0.55–0.67 dL/g. High molecular weight PET fiber grades for specialized yarns like tyre cord have inherent viscosities exceeding 0.95 dL/g. Bottle-grade PET has a "glass-clear" appearance when it is amorphous. A molecular weight of 24,000 to 36,000 g/mol on average corresponds to an inherent viscosity of 0.75 to 1.00 dL/g. The intrinsic viscosity of the common bottle grade is 0.80 dL/g. Solid additives with defined particle sizes and particle-size distributions, such as SiO2 or clay, are added to products to lessen their sticking tendency [3].

The total amount of virgin plastics produced to this point is thought to be 8300 million metric tonnes (Mt). Approximately 6300 Mt of plastic garbage has been produced as of 2015; just 9% of this material was recycled, 12% was burned, and 79% was left to pile in landfills or the environment. By 2050, 12,000 Mt of plastic garbage will be in landfills or the environment, depending on how waste is managed and produced now [4]. Although the majority of plastics are non-degradable and take a very long time to break down—possibly a hundred years—no one is quite sure when this happens in landfills. Four different pathways i.e. primary recycling, secondary recycling, chemical recycling, and incineration, through which PET polymers can be recycled [5]. Post-consumer plastic recycling rates are often relatively low. PET is one of the materials that is recycled the most; in Europe, over 57% of PET bottles were recycled in 2019 [6]. In essence, PET recycling methods are : (a.) Pre treatment or contamination removal (b.) Mechanical/Physical Treatment (c.) Chemical Recycling (d.) Incineration [5]. Among the chemical PET recycling processes (a.) Hydrolysis (b.) Methanolysis (c.) Glycolysis (d.) Ammonolysis are industrially popular [7]. Hydrolysis of PET has been at the center of attention during the last few years for the fact that this chemical pathway converts waste PET to Terephthalic Acid (TPA) and Ethylene G;ycol (EG). TPA and EG being the immediate precursor of PET, hydrolysis is drawing significant interest [5],[8]. Usually alkaline hydrolysis processes are carried out at 1-20 wt% of NaOH or KOH in presence of an aqueous or non-aqueous solvent [5]. Major disadvantage in this process is high temperature and pressure requirements. Oku et al [9] investigated the alkali-decomposition (depolymerization) of poly(ethylene terephthalate) (PET) in a solvent mixture of ethanol and ether (dioxane, tetrahydrofuran, or dimethoxyethane). When dioxane (10 vol%) was added as a co-solvent in the reaction mixture, the time for full breakdown (>96%) of solid PET with NaOH in methanol at 60°C was 40 min, while 7 h without dioxane. Product disodium terephthalate quantitatively precipitated in the medium and was quickly separated. Ethylene glycol (EG) was extracted from the filter by distillation, and for practical purposes, the majority of the filtrate was repeatedly used as the reaction medium. Different types of genuine PET plastic trash were subjected to a two-step aqueous alkaline hydrolysis in Ügdüler, Sibel, et al's investigation under benign circumstances (80 °C at atmospheric pressure). To optimize the product yield, reaction parameters such as temperature (50-80 °C), ethanol to water ratio (20-100 vol%), NaOH quantity (5-15 wt%), and stirring rate (250-500 rpm) have been tuned. Product yields on a mass basis of around 95% have been attained in less than 20 minutes under ideal circumstances (60 : 40 vol% EtOH : H2O, 5 wt% NaOH, and at 80 °C) [8]. Hydrolysis as an alternative process is occasionally abandoned since salt will always accumulate, although it may be carried out under moderate circumstances and can handle severely polluted post-consumer waste. Furthermore, the resulting monomers frequently have greater yields and purity.

Method	Catalyst	Temp. (°C)	Pressure (bar)	Time (hr)	Yield(%)	Ref.
Hydrolysis	None	200	1	1	97.9	[12}
	CycloHexylamine	90	1	2	85.1	
	None	110	1	0.5	89	
	None	99	1	2.5	85	
	Tetrabutyl ammoniu	90	1	1	99	

	m bromide					
Glycolysis	Zinc acetate	196	1	2	66	
	Tetragonal	260	5	1.5	92.2	
	None	300	11	0.4 - 0.8	0.3	
	Zinc Sulfate	80-200	1	15	25	
	Titanium Chloride	196	1	9	72	
Methanolysis	None	270	1 - 150	1.5	60	
	None	300 - 350	200	2	80	
	Zinc Acetate	250 - 270	85-140	1	60 - 95	
	None	300	9.8	1.5	80	
	Aluminum triisopropoxide	200	Not Mentioned	2	88	
Hydrolysis	None	60	1	0.6	96	[9]
	None	80	1	0.25	95	[8]
Ethylene Glycol +LDH	LDH	198	1	0.16	100	[10]
Solvent : Ethanolamine	None	200	1	0.16	91	[11]

On Micro and Nano Plastics Detection and Separation :

Detection, Separation and degradation of microplastic is in its infancy. As per scopus data, till 2020, there were less than 200 papers having term microplastic and polystyrene.

Current research on microplastics lack reliable data on the concentration of microsized synthetic polymers in different environments. This is due to the fact that the scientific community is not at the stage to reach an agreement on any standard operation protocol for the microplastic sampling and consistent detection methods [25]. Microplastic samples are collected from marine/aquatic environments by nets of suitable mesh size. Several density based floatation methods [27], [28] also have been tried.

Most popular detection method for microplastics is dye adsorption on the plastic surface. Staining microplastics with Nile Red and irradiating the tagged plastic cluster with blue light facilitates the detection and quantification of microplastics having submicron size . Nile Red is known as Nile blue oxazone is a solvatochromic dye. It is a lipophilic stain. Having solvatochromic property Nile red can be utilized for different plastic clusters of various surface polarities.

As Nile Red is susceptible to natural hydrophobic particles, it is hardly possible to detect microplastics in natural samples [49]. Da Silva et al [29] showed that it is possible to differentiate microplastic excitation in saltwater or sand samples.

Bruno et al [50] demonstrated a micro-optofluidic device to identify 1-100 μm size range plastics. In this study, density separation and organic substance treatment is opted at first.

Then the supernatant is vacuum filtered. The filter with microplastic is then put under FTIR/Raman microscope.

FITC and Safranine T dyes were selected to stain microplastics. This is a highly efficient and rapid method for the detection of PE, PVC, PS, PET microplastics [15]. Commercially available different textile dyes have been used to label microplastics. Different disperse dyes which are used in the textile industry can be a good marker to identify microplastics [51] .

Fluorescent properties of molecular rotors have also been studied for the detection of microplastics. 9-(2,2-dicyanovinyl)julolidine (DCVJ), has been used to detect and quantify polystyrene nanoplastics [52]. Molecular rotors are a group of fluorescent molecules that form twisted intramolecular charge transfer (TICT) states upon photoexcitation and therefore exhibit two competing deexcitation pathways: fluorescence emission and non-radiative deexcitation from the TICT state [18].

While micro-FTIR, Pyrolysis-GC, micro-Raman [26] are very popular method to detect microplastics, it has been recently established that hyperspectral imaging can also be employed to detect label free detection of microplastics. [30] [31]

While it comes to separation of microplastics from marine/aquatic environments several methods of Membrane Filtration to adsorption have been studied. MP's from landfill leachate has been significantly reduced by membrane separation techniques by Bing-Jie and colleagues [32]. PVC microplastics from waste water can be separated by employing Membrane Bioreactor [33]. One of the well studied fields on microplastic separation is coagulation-flocculation/floatation methods [34]. Coagulation-Flocculation is a heterogeneous separation method, which recently showed high efficiency output for MP removal [35] [36]. As microplastics show greater affinity towards different pollutants, researchers have manipulated these characteristics for the removal of MP's from different samples employing the principles of adsorption [37]. Some of the similar studies show excellent removal of MP's [38]. Tammelin et al used Cellulose Nanofiber hydrogels for the removal of colloidal nano and microplastics. CNF, a biocompatible material, shows fabulous adsorption towards nano and microplastics. This study also designed an application oriented microfluidic device for the NP and MP removal. [39]

Degradation of plastics by microbial and/or enzymatic processes is a promising technique to depolymerize waste petro-plastics into monomers for recycling, or mineralize them into carbon dioxide, water, and new biomass, with concomitant production of higher-value bioproducts [40][41]. Biodegradation of plastics involves excretion of extracellular enzymes by the microorganism, attachment of enzymes to the surface of plastic, hydrolysis to short polymer intermediates, which are ultimately assimilated by microbial cells as carbon source to release CO2. Despite the fact that these plastics represent non-natural chemicals, several microorganisms capable of metabolizing these polymers have been identified in recent years. Over 90 microorganisms, including bacteria and fungi, have been known to degrade petroleum-based plastics [42] mostly in vitro condition.

In recent years, an increasing number of bacterial isolates that can degrade MPs have been identified, and their degradation properties and effects on MPs have received increasing attention. In a study by Auta [43], two pure bacterial cultures were obtained from mangrove sediment and used for PP MP degradation. After 40 days of incubation, the weight loss of PP MP promoted by Rhodococcus sp. strain 36 and Bacillus sp. strain 27 was 6.4 and 4.0%, respectively.

Degradation by synthetic polymer is an emerging domain of plastic waste mitigation processes [44] and holds the key to degrade plastics in its environmental condition without causing harm to the environment [45]. Currently extensive studies are being carried out to investigate, recalibrate and optimize biologically plastics degradation strategies and different environmental conditions [46], [47], [48].

References

[1] López-Fonseca, Rubén, et al. "Kinetics of catalytic glycolysis of PET wastes with sodium carbonate." *Chemical engineering journal* 168.1 (2011): 312-320.

[2] Sinha, Vijaykumar, Mayank R. Patel, and Jigar V. Patel. "PET waste management by chemical recycling: a review." *Journal of Polymers and the Environment* 18.1 (2010): 8-25.

[3] Long, Timothy E., and John Scheirs, eds. *Modern polyesters: chemistry and technology of polyesters and copolyesters*. John Wiley & Sons, 2005.

[4] Geyer, Roland, Jenna R. Jambeck, and Kara Lavender Law. "Production, use, and fate of all plastics ever made." *Science advances* 3.7 (2017): e1700782.

[5] Al-Sabagh, A. M., et al. "Greener routes for recycling of polyethylene terephthalate." *Egyptian Journal of Petroleum* 25.1 (2016): 53-64.

[6] Walker, Theodore W., et al. "Recycling of multilayer plastic packaging materials by solvent-targeted recovery and precipitation." *Science advances* 6.47 (2020): eaba7599.

[7] Wei, Ren, et al. "Possibilities and limitations of biotechnological plastic degradation and recycling." *Nature Catalysis* 3.11 (2020): 867-871.

[8] Ügdüler, Sibel, et al. "Towards closed-loop recycling of multilayer and coloured PET plastic waste by alkaline hydrolysis." *Green chemistry* 22.16 (2020): 5376-5394.

[9] Hu, Lian-Chun, et al. "Alkali-decomposition of poly (ethylene terephthalate) in mixed media of nonaqueous alcohol and ether. Study on recycling of poly (ethylene terephthalate)." *Polymer journal* 29.9 (1997): 708-712.

[10] Sharma, Vivek, Priyanka Shrivastava, and D. D. Agarwal. "Degradation of PET-bottles to mono hydroxyethyl terephthalate (MHT) using ethylene glycol and hydrotalcite." *Journal of Polymer Research* 22.12 (2015): 1-10.

[11] Bäckström, Eva, Karin Odelius, and Minna Hakkarainen. "Ultrafast microwave assisted recycling of PET to a family of functional precursors and materials." *European Polymer Journal* 151 (2021): 110441.

[12] G. P. Karayiannidis , A. P. Chatziavgoustis and D. S. Achilias , Poly(ethylene terephthalate) recycling and recovery of pure terephthalic acid by alkaline hydrolysis, *Adv. Polym. Technol.*, 2002, 4 , 250 —259

[13] S. Mishra and A. S. Goje , Chemical recycling, kinetics, and thermodynamics of alkaline depolymerization of waste poly(ethylene terephthalate) (PET), Polym. React. Eng., 2003, 11 , 963 —987 .

[14] M. Yamashita and H. Mukai , Alkaline Hydrolysis of Polyethylene Terephthalate at Lower Reaction Temperature, Sci. Eng. Rev. Doshisha Univ., 2011, 52 , 143 —148.

[15] S. Mishra , V. S. Zope and A. S. Goje , Kinetic and thermodynamic studies of depolymerisation of poly(ethylene terephthalate) by saponification reaction, Polym. Int., 2002, 51 , 1310 —1315.

[16] H. I. Khalaf and O. A. Hasan , Effect of quaternary ammonium salt as a phase transfer catalyst for the microwave depolymerization of polyethylene terephthalate waste bottles, Chem. Eng. J., 2012, 192 , 45 —48.
[17] R. López-Fonseca , M. P. González-Marcos , J. R. González-Velasco and J. I. Gutiérrez-Ortiz , A kinetic study of the depolymerisation of poly(ethylene terephthalate): By phase transfer catalyzed alkaline hydrolysis, J. Chem. Technol. Biotechnol., 2009, 84 , 92 —99 .

[18] M. Imran , D. H. Kim , W. A. Al-Masry , A. Mahmood , A. Hassan , S. Haider and R. Shadid Mahmood , Manganese-, cobalt-, and zinc-based mixed-oxide spinels as novel catalysts

for the chemical recycling of poly(ethylene terephthalate) via glycolysis, Polym. Degrad. Stab., 2013, 98 , 904 —915 .

[19] M. Imran , B. K. Kim , M. Han , B. G. Cho and D. H. Kim , Sub-and supercritical glycolysis of polyethylene terephthalate (PET) into the monomer bis(2-hydroxyethyl) terephthalate (BHET), Polym. Degrad. Stab., 2010, 95 , 1686 —1693.

[20] M. Ghaemy and K. Mossadegh , Depolymerisation of poly(ethylene terephthalate) fiber wastes using ethylene glycol, Polym. Degrad. Stab., 2005, 90 , 570 —576.

[21] H. A. Essawy , M. E. Tawfik and N. H. Elsayed , Effect of addition of glycolysis products of poly(ethyleneterephthalate) wastes to urea-formaldehyde resin on its adhesion performance to wood substrates and formaldehyde emission, J. Appl. Polym. Sci., 2012, 123 , 2377 —2383

[22] M. Genta , T. Iwaya , M. Sasaki , M. Goto and T. Hirose , Depolymerization mechanism of poly(ethylene terephthalate) in supercritical methanol, Ind. Eng. Chem. Res., 2005, 44 , 3894 —3900.

[23] M. Goto , H. Kawamoto , A. Kodama , T. Hirose and S. Nagaoka , Depolymerization of polyethylene terephthalate in supercritical methanol, J. Phys.: Condens. Matter, 2002, 14 , 11427 —11430.

[24] Y. Yang , Y. Lu , H. Xiang , Y. Xu and Y. Li , Study on methanolytic depolymerization of PET with supercritical methanol for chemical recycling, Polym. Degrad. Stab., 2002, 75 , 185 —191.

[25] M. Genta , T. Iwaya , M. Sasaki and M. Goto , Supercritical methanol for polyethylene terephthalate depolymerization: Observation using simulator, Waste Manage., 2007, 27 , 1167 —1177

[26] Löder, Martin GJ, and Gunnar Gerdts. "Methodology used for the detection and identification of microplastics—a critical appraisal." *Marine anthropogenic litter* (2015):

201-227.

[27] Han, Xiaoxin, Xueqiang Lu, and Rolf D. Vogt. "An optimized density-based approach for extracting microplastics from soil and sediment samples." *Environmental Pollution* 254 (2019): 113009.

[28] Li, Chengtao, et al. "A commonly available and easily assembled device for extraction of bio/non-degradable microplastics from soil by flotation in NaBr solution." *Science of The Total Environment* 759 (2021): 143482.

[29] Costa, Camila QV, et al. "Fluorescence sensing of microplastics on surfaces." *Environmental Chemistry Letters* 19.2 (2021): 1797-1802.

[30] Piarulli, Stefania, et al. "Rapid and direct detection of small microplastics in aquatic samples by a new near infrared hyperspectral imaging (NIR-HSI) method." *Chemosphere* 260 (2020): 127655.

[31] Zhu, Chunmao, et al. "Characterization of microplastics on filter substrates based on hyperspectral imaging: Laboratory assessments." *Environmental Pollution* 263 (2020): 114296.

[32] Sun, Jing, et al. "Revisiting microplastics in landfill leachate: Unnoticed tiny microplastics and their fate in treatment works." *Water Research* 190 (2021): 116784.

[33] Li, Lu, et al. ``Performance evaluation of MBR in treating microplastics polyvinyl chloride contaminated polluted surface water." *Marine Pollution Bulletin* 150 (2020): 110724.

[34] Wang, Chong-qing, et al. "Flotation separation of waste plastics for recycling—A review." *Waste Management* 41 (2015): 28-38.

[35] Perren, William, Arkadiusz Wojtasik, and Qiong Cai. "Removal of microbeads from wastewater using electrocoagulation." *ACS omega* 3.3 (2018): 3357-3364.

[36] Ma, Baiwen, et al. "Removal characteristics of microplastics by Fe-based coagulants during drinking water treatment." *Journal of Environmental Sciences* 78 (2019): 267-275.

[37] Joo, Sung Hee, et al. "Microplastics with adsorbed contaminants: Mechanisms and Treatment." *Environmental Challenges* 3 (2021): 100042.

[38] Wang, Jun, et al. "Adsorption and thermal degradation of microplastics from aqueous solutions by Mg/Zn modified magnetic biochars." *Journal of hazardous materials* 419 (2021): 126486.

[39] Leppänen, Ilona, et al. "Capturing colloidal nano-and microplastics with plant-based nanocellulose networks." *Nature Communications* 13.1 (2022): 1-12.

[40] Grima, Sophie, et al. "Aerobic biodegradation of polymers in solid-state conditions: a review of environmental and physicochemical parameter settings in laboratory simulations." *Journal of Polymers and the Environment* 8.4 (2000): 183-195.

[41] Montazer, Zahra, Mohammad B. Habibi Najafi, and David B. Levin. "Microbial degradation of low-density polyethylene and synthesis of polyhydroxyalkanoate polymers." *Canadian journal of microbiology* 65.3 (2019): 224-234.

[42] Jumaah, Omar Saad. "Screening of plastic degrading bacteria from dumped soil area." *IOSR J. Environ. Sci. Toxicol. Food Technol* 11 (2017): 93-98.

[43] Auta, Helen Shnada, et al. "Growth kinetics and biodeterioration of polypropylene microplastics by Bacillus sp. and Rhodococcus sp. isolated from mangrove sediment." *Marine Pollution Bulletin* 127 (2018): 15-21.

[44] Shah, Aamer Ali, et al. "Biological degradation of plastics: a comprehensive review." Biotechnology advances 26.3 (2008): 246-265.

[45] Danso, Dominik, Jennifer Chow, and Wolfgang R. Streit. "Plastics: environmental and biotechnological perspectives on microbial degradation." *Applied and environmental*

microbiology 85.19 (2019): e01095-19.

[46] Ahmed, Temoor, et al. "Biodegradation of plastics: current scenario and future prospects for environmental safety." *Environmental Science and Pollution Research* 25.8 (2018): 7287-7298.

[47] Matjašič, Tjaša, et al. "Critical evaluation of biodegradation studies on synthetic plastics through a systematic literature review." *Science of The Total Environment* 752 (2021): 141959.

[48] Anjana, K., et al. "Review on plastic wastes in marine environment–Biodegradation and biotechnological solutions." *Marine Pollution Bulletin* 150 (2020): 110733.

[49] Maes, Thomas, et al. "G.(2017). A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red." *Scientific Reports* 7.

[50] Elsayed, Ahmed A., et al. "A microfluidic chip enables fast analysis of water microplastics by optical spectroscopy." *Scientific reports* 11.1 (2021): 1-11.

[51] Karakolis, Evan G., et al. "Fluorescent dyes for visualizing microplastic particles and fibers in laboratory-based studies." *Environmental Science & Technology Letters* 6.6 (2019): 334-340.

[52] Moraz, Angélique, and Florian Breider. "Detection and Quantification of Non Labeled Polystyrene Nanoparticles Using a Fluorescent Molecular Rotor." *Analytical Chemistry* 93.45 (2021): 14976-14984.

Degradation of Polyethylene Terephthalate (PET) at Room Temperature and Ambient Pressure Condition

The total amount of virgin plastics produced to this point is thought to be 8300 million metric tonnes (Mt). Approximately 6300 Mt of plastic garbage has been produced as of 2015; just 9% of this material was recycled, 12% was burned, and 79% was left to pile in landfills or the environment. By 2050, 12,000 Mt of plastic garbage will be in landfills or the environment, depending on how waste is managed and produced now [1]. Four different pathways i.e. primary recycling, secondary recycling, chemical recycling, and incineration, through which PET polymers can be recycled [2]. Post-consumer plastic recycling rates are often relatively low. PET is one of the materials that is recycled the most; in Europe, over 57% of PET bottles were recycled in 2019 [3]. In essence, PET recycling methods are : (a.) Pre treatment or contamination removal (b.) Mechanical/Physical Treatment (c.) Chemical Recycling (d.) Incineration [5]. Among the chemical PET recycling processes (a.) Hydrolysis (b.) Methanolysis (c.) Glycolysis (d.) Ammonolysis is industrially popular [4].

Hydrolysis of PET has been recently at the center of attention for the fact that this chemical pathway converts waste PET to Terephthalic Acid (TPA) and Ethylene G;ycol (EG) directly. TPA and EG being the immediate precursor of PET, hydrolysis is drawing significant interest [5],[8]. Usually alkaline hydrolysis processes are carried out at 1-20 wt% of NaOH or KOH in presence of an aqueous or non-aqueous solvent [2]. Major disadvantage in this process is high temperature and pressure requirements. PET hydrolysis is influenced by (a.)reaction temperatures, ideally over Tg; (b) water absorbency, which is closely connected to temperature; (c) crystallinity; (d) orientation of polymer chains, either in order or amorphous; and (e) surface topology, in general [7]. To facilitate the degradation via alkaline hydrolysis below the glass transition temperature one must take into account the properties of the solvents used, Gallagher et al showed [8].. Oku et al [5] investigated the alkali-decomposition (depolymerization) of poly(ethylene terephthalate) (PET) in a solvent mixture of ethanol and ether (dioxane, tetrahydrofuran, or dimethoxyethane). When dioxane (10 vol%) was added as a co-solvent in the reaction mixture, the time for full breakdown (>96%) of solid PET with NaOH in methanol at 60°C was 40 min, while 7 h without dioxane. Product disodium terephthalate quantitatively precipitated in the medium and was quickly separated. Different types of genuine PET plastic trash were subjected to a two-step aqueous alkaline hydrolysis in Ügdüler, Sibel, et al's investigation under benign circumstances (80 °C at atmospheric pressure). To optimize the product yield, reaction parameters such as temperature (50-80 °C), ethanol to water ratio (20-100 vol%), NaOH quantity (5-15 wt%), and stirring rate (250-500 rpm) have been tuned. Product yields on a mass basis of around 95% have been attained in less than 20 minutes under ideal circumstances (60 : 40 vol% EtOH : H2O, 5 wt% NaOH, and at 80 °C) [8]. Hydrolysis as an alternative process is occasionally abandoned since salt will always accumulate, although it may be carried out under moderate circumstances and can handle severely polluted post-consumer waste. Furthermore, the resulting monomers frequently have greater yields and purity.

In this study, we have shown that correct choice of co-solvents in alkaline hydrolysis of PET can completely degrade the polyester into its constituents even in room temperature and ambient pressure conditions. **To the best of our knowledge, we report the degradation of PET plastic waste at room temperature and atmospheric pressure for the first time**. **We have been able to degrade almost 100% of PET flakes within 4hr using NaOH assisted hydrolysis in presence of Acetonitrile and Ethanol at 1:3 proportion and 1:10 (w/v) proportion NaOH:Solvent .** We have also investigated several other solvents to carry out PET degradation at similar conditions.

Materials and Method :

Sodium hydroxide (NaOH), Acetonitrile (MeCN), Ethanol (EtOH), Hydrochloric Acid (HCl) have been supplied by Sigma Aldrich (Merck). Whatman Filter paper has been purchased from the same vendor. For PET flakes cold drinks PET bottles have been cleaned and dried and then cut into 2 mm x 2mm size with the help of a mechanical shredder. All chemical compounds have been used without any purification.

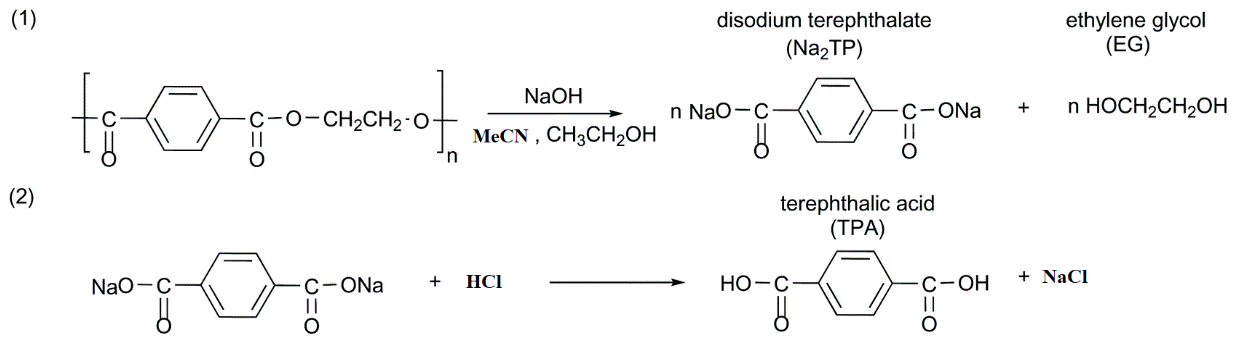
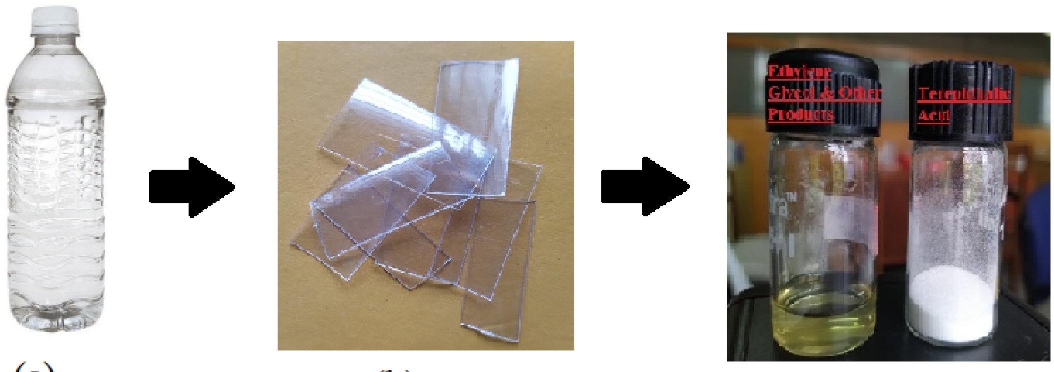


Fig. Alkaline Hydrolysis Reaction

Hydrolysis :

10ml solvent consisting of MeCN and EtOH was taken in 1:3 ratio in a wolf flask. 1 gm of PET flakes were put into the reactor. 1 gm of NaOH pellets were added into the solvent. Magnetic stirrer was set at 800 rpm. Water baths at constant temperature were passed around the reactor. Same reaction was carried out for 1hr, 2hr, 3 hr and 4hr separately. In each case, after the mentioned time, 50 ml chilled water is added to stop the reaction and titrated by 0.4 (N) HCl until the pH reaches 3.5-4.0. A white thick solution will be formed after the titration. Then it was filtered using a vacuum filter and Whatman filter paper of ultrafiltration pore range. The cake is dried and kept away from moisture for characterisation. The filtrate is put into another wolf flask for distillation. Heating the filtrate at upto 110 °C will remove MeCN, Ethanol and Water separately. The remaining bottom is rich with Ethylene Glycol. The bottom product is fed in GC-MS for characterisation purposes.

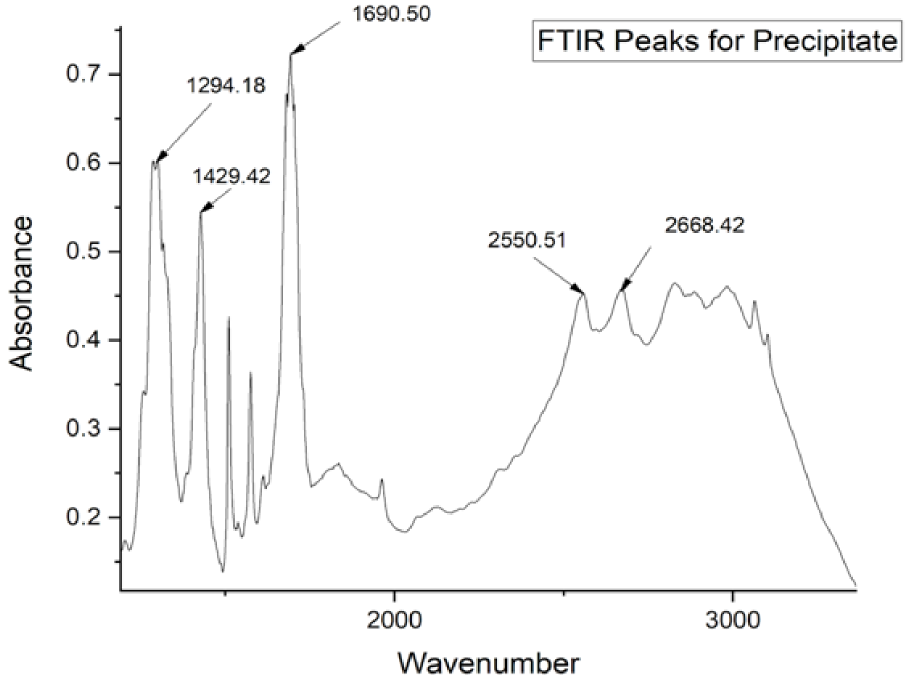


(a) (b) (c)

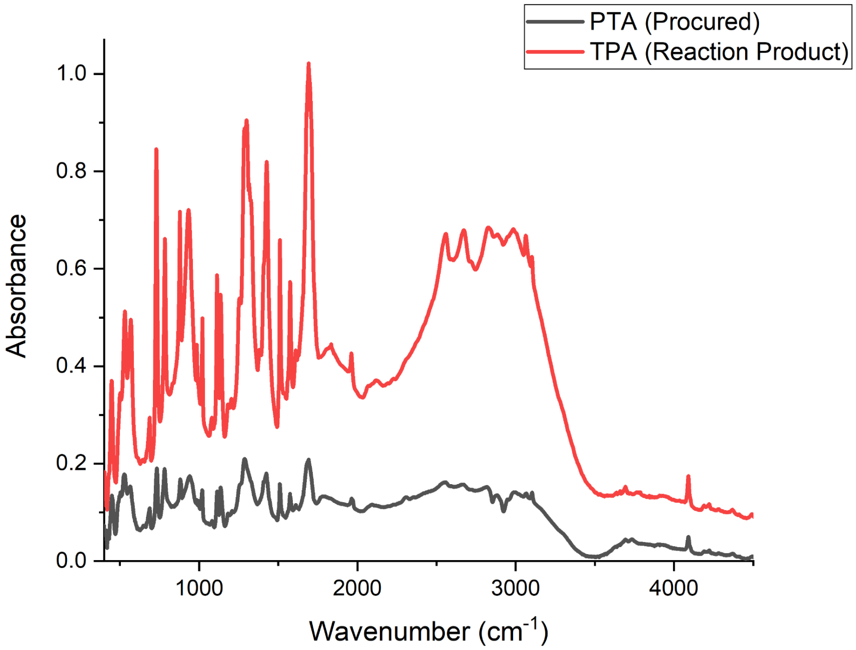
Fig. (a) Waste PET bottle (b) PET Flakes (C) EG and TPA

Results and Discussion :

FTIR data of Filter Cake confirms the yield of TPA



(a)



(b)

Fig. (a) FTIR spectrum of Terephthalic Acid (TPA) with characteristic peaks. (b) FTIR of filter cake along with a reference spectrum that has been obtained from analytical grade Pure terephthalic Acid purchased from Sigma Aldrich (Merck).

It is evident that IR Spectroscopy of TPA matches with the filter cake obtained from hydrolysis reaction [9]. Specification bonds at 2500-3250 cm-1 are related to the carboxylic group, 1685 cm-1 are related to the carbonyl group and 1574-1425 cm-1 are related to the aromatic ring. These results have a good match with the reference data related to analytical grade purchased Pure terephthalic Acid showing that the purity of the product in this method is passable [10].

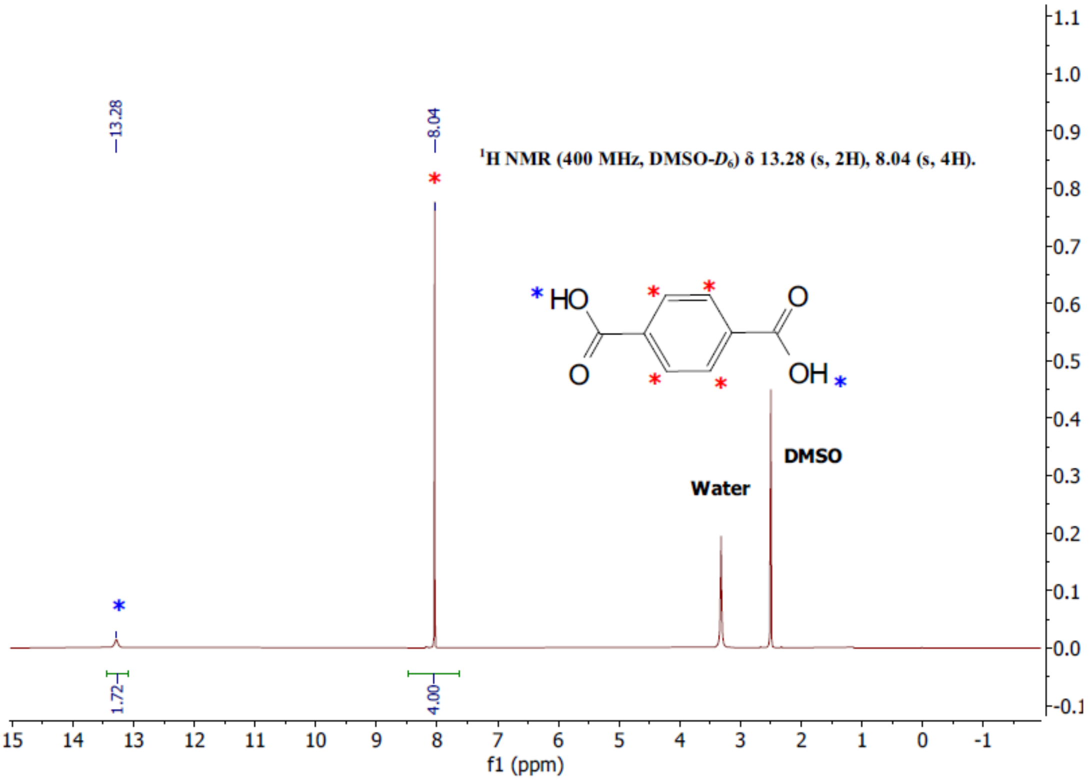


Fig. 1H-NMR of Filter Cake.

1H-NMR of filter cake confirmed the presence of Benzene ring and carboxylic hydrogens and the mentioned peaks in above figure.

GC-MS Data of the Filtrate Confirms the Presence of Ethylene Glycol

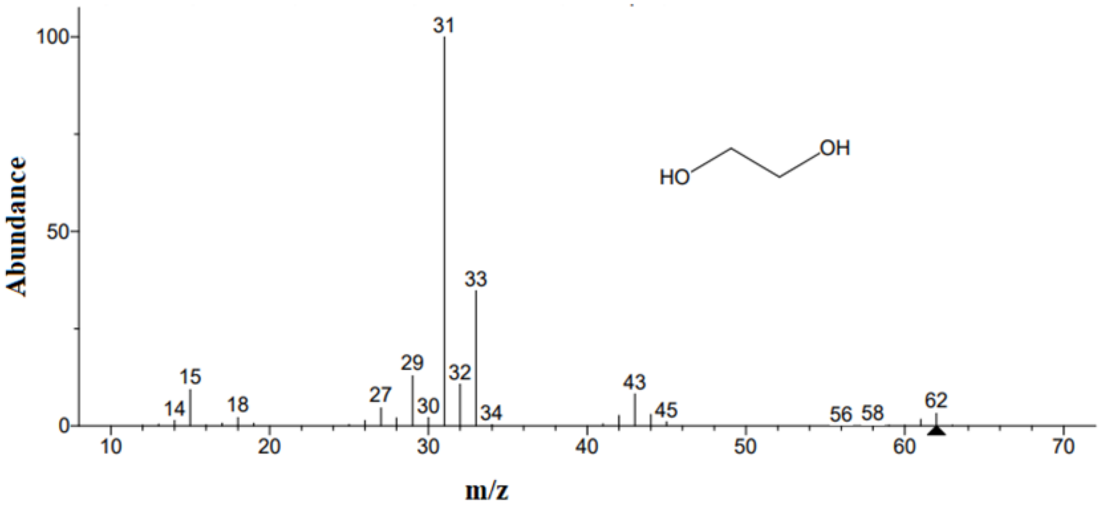


Fig. : GC-MS data of the bottom distillate confirms the presence of Ethylene glycol having m/z value 62.

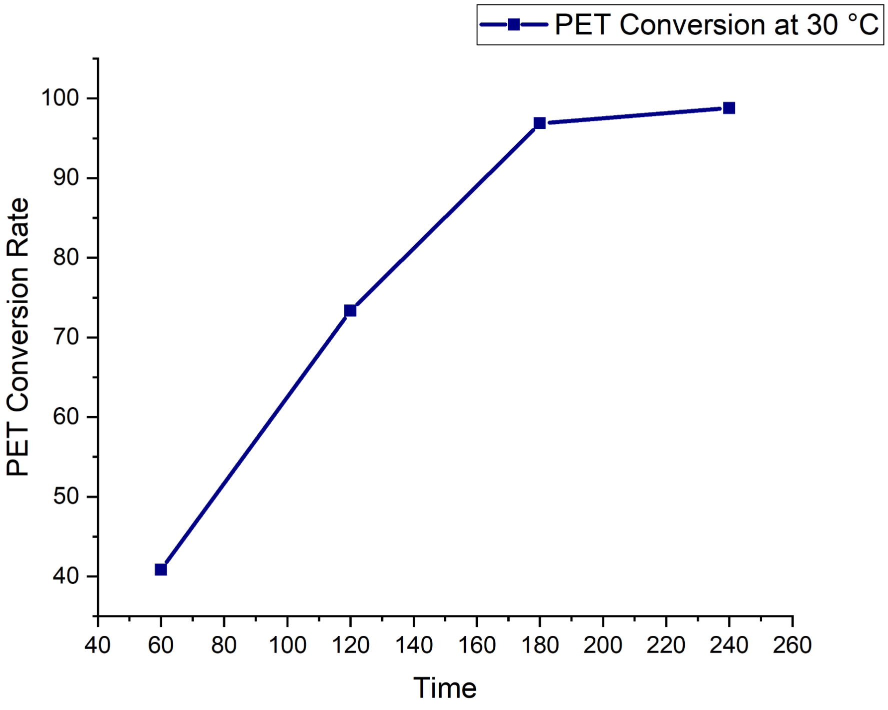


Fig. PET Degradation rate with respect to time at atmospheric pressure and room temperature.

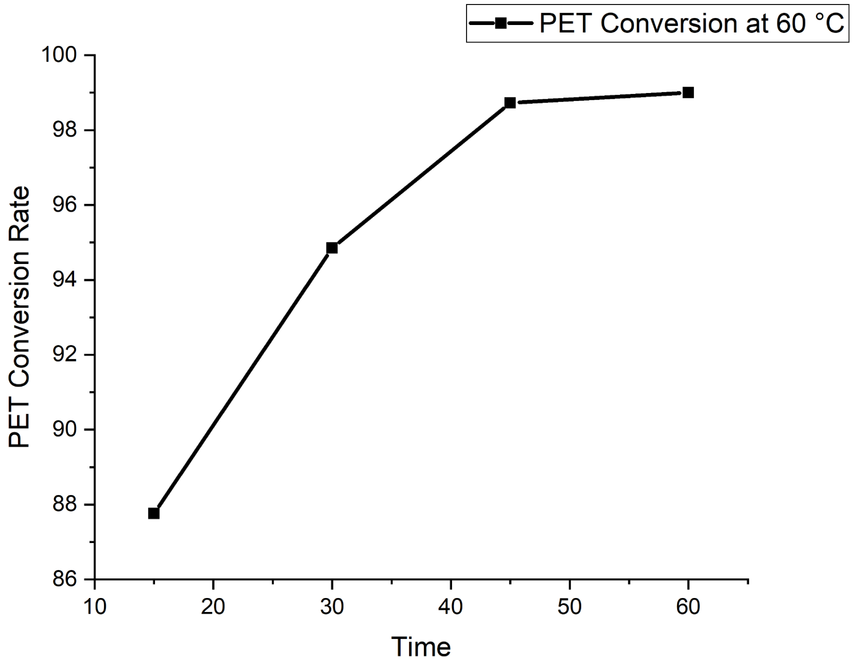


Fig. PET Degradation Rate at 60 degree C Temperature w.r.t Time

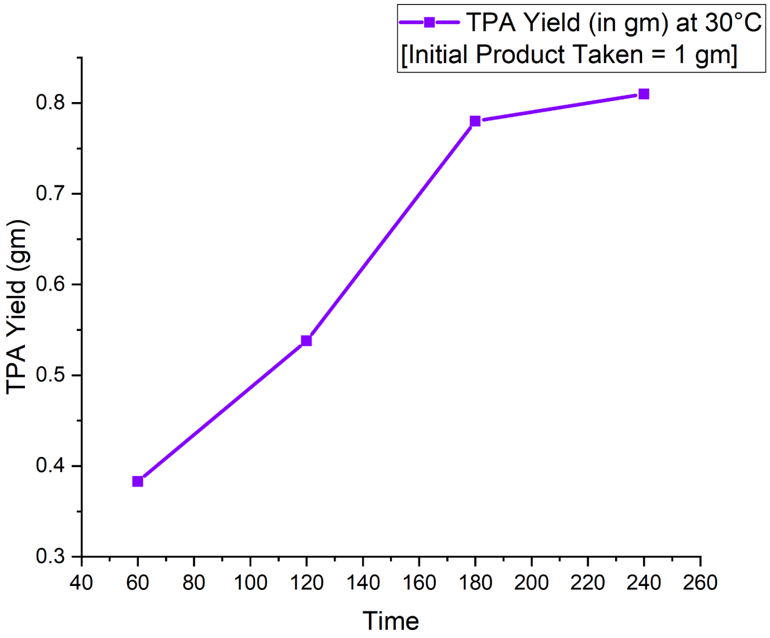


Fig. : Terephthalic Acid Yield w.r.t Time at room Temperature.

Hydrolysis of PET with different Co-Solvents and Degradation Rate. All the following Reaction have been studied for their degradation efficiency:

No..	Solvent Combination	Reaction Temperature	Reaction Time	% Degradation
01.	Ethanol : Acetonitrile	30 °C	4 hr	98.81%
02.	Ethanol : Acetonitrile	60 °C	1 hr	99.80%
03.	Ethanol : Dioxane	60 °C	1 hr	85.35%
04.	Ethanol : Dioxane : Water	60 °C	1 hr	63 %
05.	Ethanol : Acetone	60 °C	1 hr	47.01
06.	Ethanol : THF	60 °C	40 mins	60.6 %
07.	Ethanol : THF (CTAB PTC)	60 °C	40 mins	63.26 %
08.	Ethanol : DMSO	60 °C	40 mins	75.2 %
09.	DMSO (Ni-Fe LDH as Catalyst)	190 °C	10 mins	100 % [to PET Oligomers]

Fig. PET Degradation Table

Yan et al [11] in their study showed by Implicit as well as Explicit Solvent Model of PET hydrolysis mechanism that the micro-solvation of explicit H2O molecules strongly influences hydrolysis mechanism by the interaction of hydrogen bonds which can stabilize different conformations and influence the exo-anomeric effect and hence the energy barrier. Compared with PET+H2O hydrolysis of ISM, the presence of explicit H2O molecules of all three ESMs has no change in hydrolysis mechanism but shows change in activation energies and reaction energies. For PET+3H2O hydrolysis, H2O(II) participates in the dissociation of H2O(I) which reduce the activation energy from 38.53 kcal/mol to 25.36 kcal/mol while H2O(III) participates in the cleavage of ester group which increases the activation energy slightly from 23.53 kcal/mol to 25.18 kcal/mol.hich can stabilize different conformations and influence the exo-anomeric effect and hence the energy barrier. Balakrishnan et al [12] showed that Increasing the ethanol content in aqueous ethanol leads to a decrease in the dielectric constant of the medium and concurrently to a decrease in the rates of saponification of esters. On the contrary, Ostwald et al [13] showed that if the solvent system is changed from water to 60% aqueous DMSO enhances the efficiency of ester cleavage by P-cyclodextrin but the origin and generality of this effect has not been established. Gallaghar et al [8] ascribed the increase in rate to the existence of both hydrophilic and hydrophobic groups in the activated complex. Because of the specific attractions of these groups, solvation of the complex should be greater in some mixtures of more polar and organic solvents than in polar solvents alone. This interesting phenomenon where the cleavage of ester bonds increases below their glass transition temperature needs further studies to propose a more compact basis on which we can visualize the reason behind the current study this chapter tries to compile.

[1] Geyer, Roland, Jenna R. Jambeck, and Kara Lavender Law. "Production, use, and fate of all plastics ever made." *Science advances* 3.7 (2017): e1700782.

[2] Al-Sabagh, A. M., et al. "Greener routes for recycling of polyethylene terephthalate." *Egyptian Journal of Petroleum* 25.1 (2016): 53-64.

[3] Walker, Theodore W., et al. "Recycling of multilayer plastic packaging materials by solvent-targeted recovery and precipitation." *Science advances* 6.47 (2020): eaba7599.

[4] Wei, Ren, et al. "Possibilities and limitations of biotechnological plastic degradation and recycling." *Nature Catalysis* 3.11 (2020): 867-871.

[5] Ügdüler, Sibel, et al. "Towards closed-loop recycling of multilayer and coloured PET plastic waste by alkaline hydrolysis." *Green chemistry* 22.16 (2020): 5376-5394.

[6] Hu, Lian-Chun, et al. "Alkali-decomposition of poly (ethylene terephthalate) in mixed media of nonaqueous alcohol and ether. Study on recycling of poly (ethylene terephthalate)."

[7] Kawai, Fusako, Takeshi Kawabata, and Masayuki Oda. "Current knowledge on enzymatic PET degradation and its possible application to waste stream management and other fields." *Applied microbiology and biotechnology* 103.11 (2019): 4253-4268.

[8] Gallagher, George A., John G. Miller, and Allan R. Day. "Solvent Effects and Ester Interchange in Basic Hydrolysis of Esters." *Journal of the American Chemical Society* 79.16 (1957): 4324-4327.

[9] Hollauer, Eduardo, M. A. Mondragon, and Victor M. Castaño. "Fourier transform infrared and Raman spectra, vibrational assignment and ab initio calculations of terephthalic acid and related compounds." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 57.5 (2001): 993-1007.

[10] Ghamary, Elmira, et al. "Recovery of Terephthalic Acid by employing magnetic nanoparticles as a solid support." *Polímeros* 28 (2018): 01-05.

[11] Yan, Zhifeng, et al. "Deeper insight into hydrolysis mechanisms of polyester/cotton blended fabrics for separation by explicit solvent models." *International Journal of Biological Macromolecules* 154 (2020): 596-605.

[12] https://www.ias.ac.in/article/fulltext/seca/080/01/0050-0056

[13] Tee, Oswald S., and John A. Enos. "Hydrolysis of p-nitrophenyl alkanoates in aqueous organic solvent mixtures. The dispersal of aggregates and the uncoiling of n-alkyl chains." *Canadian journal of chemistry* 66.12 (1988): 3027-3030.

A Cohesive Strategy For Synthesis, Characterisation, Detection and Separation of Microplastic and Nanoplastic Particles : Biological Impacts and Solutions

Introduction

Worldwide plastic usage is at an all time high. The ultimate destination for most disposed plastic is in the oceans. Plastic waste in the oceans comes from many sources, but plastic bottles are the third most common source, according to a survey by the USNPS and NOAA. [1]

Despite the common notion that plastics are resistant to breakdown, they are constantly degraded in the oceans by such abiotic processes as thermal degradation, photochemical degradation,[2] degradation due to mechanical abrasion.[3] Thus microplastic particles and nanoplastic particles are found extensively in marine organisms[4] and in birds that feed on marine organisms.[5]

In vitro synthesis of microplastic particles and nanoplastic particles has been done via two methods – the laser ablation method[6] and the Phase Separation method (trifluoroacetic acid method).[7]

In this paper, we have synthesized microplastic particles and nanoplastic particles by a novel modification via treatment of PET with TCA (Trichloroacetic ACid). The resulting microplastic and nanoplastic particles have been conjugated with Nile Red, a fluorescent dye, and then uptake through bioaccumulation has been demonstrated in brine shrimp (*Artemia franciscana)* through fluorescence analysis under a confocal microscope.

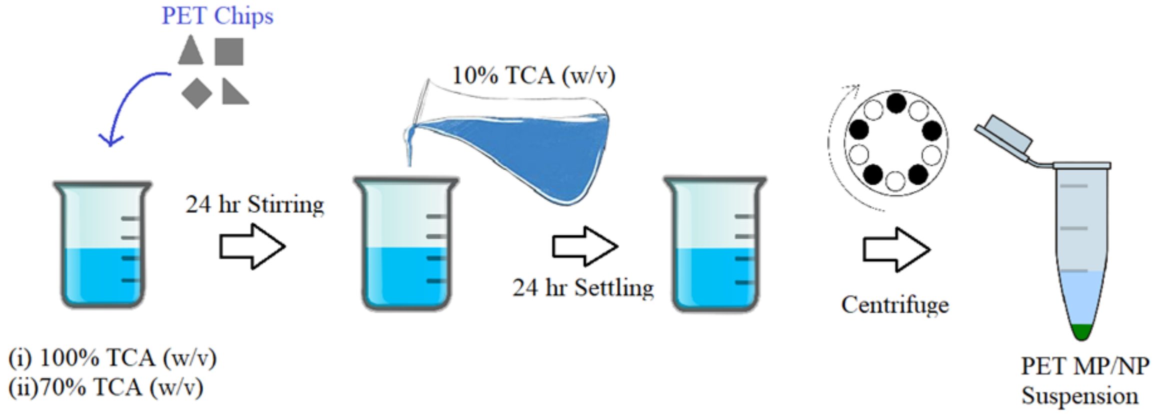
We have further demonstrated the separation of microplastic particles and nanoplastic particles from aqueous solution by Layered Double Hydroxide modified Polysulfone membrane. Removal of micro/Nano plastics of certain size ranges has been checked using dynamic light scattering method and UV spectroscopy. This may be a viable strategy to reduce concentrations of microplastic and nanoplastic particles in drinking water.

Experimental Procedures

PET nanoparticle preparation

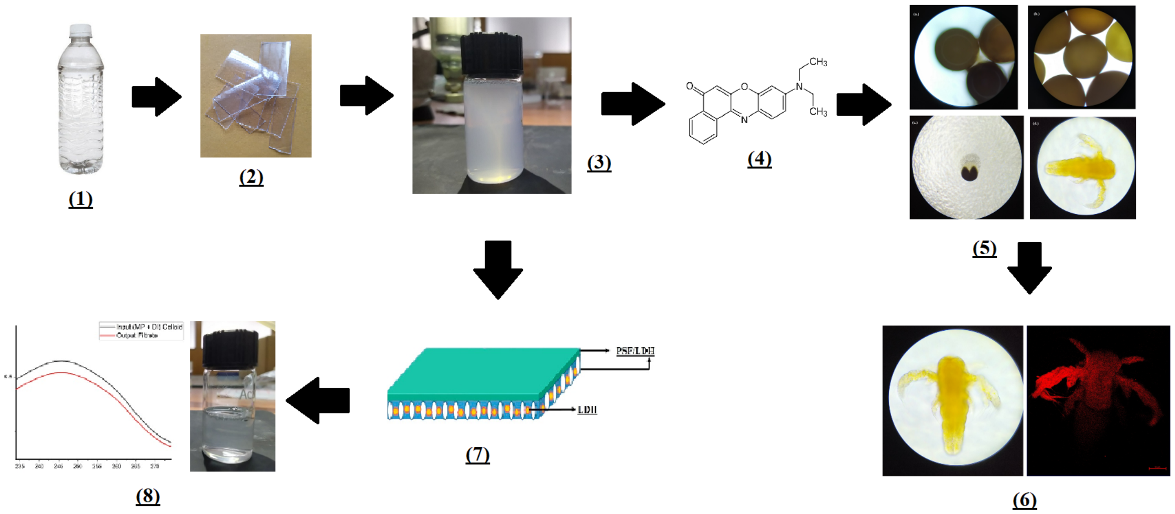
Polyethylene terephthalate (PET) is a polymer of terephthalic acid and ethylene glycol. PET flakes have been used to produce microplastic particles and nanoplastic particles. First, post-consumer waste PET bottles are cleaned and dried. Then, they are finely cut into small pieces (2mm x 2mm). One gram of the PET particles was dissolved in 10 mL of concentrated trichloroacetic acid solution (TCA) (90% v/v) at 60 °C and stirred until complete dissolution (6 hr approximately). After dissolution, the solution was kept overnight. In order to precipitate the micro/nanoparticles, 10 mL of a diluted aqueous solution of trichloroacetic acid (20% v/v) was added to the initial mixture under vigorous stirring and kept stirred for 2 hours, and then centrifuged at 2500 g for 30 min. This was repeated 3-4 times until the pH became neutral. Lately it was suspended in 0.5% BSA and 0.5% SDS (w/v) separately.

Both the pellet and the supernatant samples were resuspended in two sets of working solutions with BSA and SDS for FTIR and DLS (dynamic light scattering) experiments. SEM images of the microparticles and nanoparticles were obtained. Stable solutions of the microparticles and nanoparticles were made at different pH values and their zeta potentials measured.[8]



Scheme : PET MP/NP Synthesis

Overview of the experimental process



[Shown in figure: 1. PET Bottle 2. PET bottle cut into chips 3. Microplastic colloidal suspension prepared by TCA digestion 4. Nile Red staining of microplastics for uptake assay 5. Light microscopic view of *Artemia franciscana* (10X, 40X) 6. Confocal view of shrimp with uptake of tagged microplastics 7. Preparation of PSF-LDH membrane with nanoparticles for filtration assay 8. UV-VIS Spectrophotometric analysis]

FTIR Analysis

In order to ensure that the process of synthesizing PET microplastic particles (MP) and nanoplastic particles (NP) did not cause any change in chemical structure, Fourier-transformed Infrared Spectroscopy was performed. For this purpose, both samples from the supernatant and the pellet obtained after centrifugation were used. The supernatant samples were labeled with the suffix 'T' and the pellet samples were labeled 'B'.

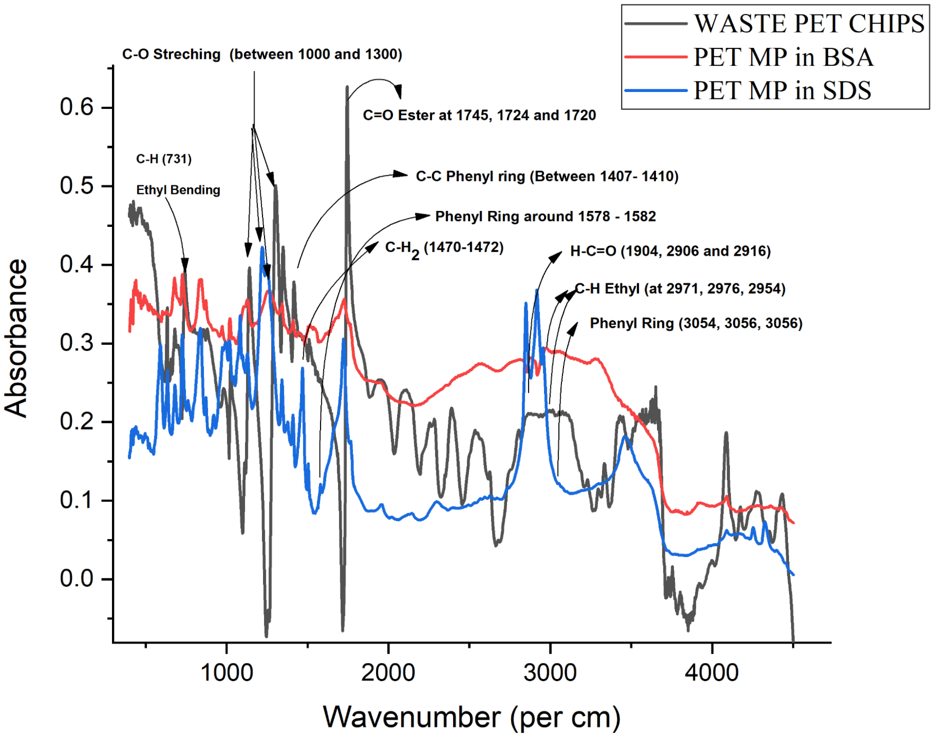


Fig. FTIR Peak Analysis of Micro/Nano plastics (MP/NP) along with PET flakes (chips) shows that no chemical/structural changes for MP/NP took place.

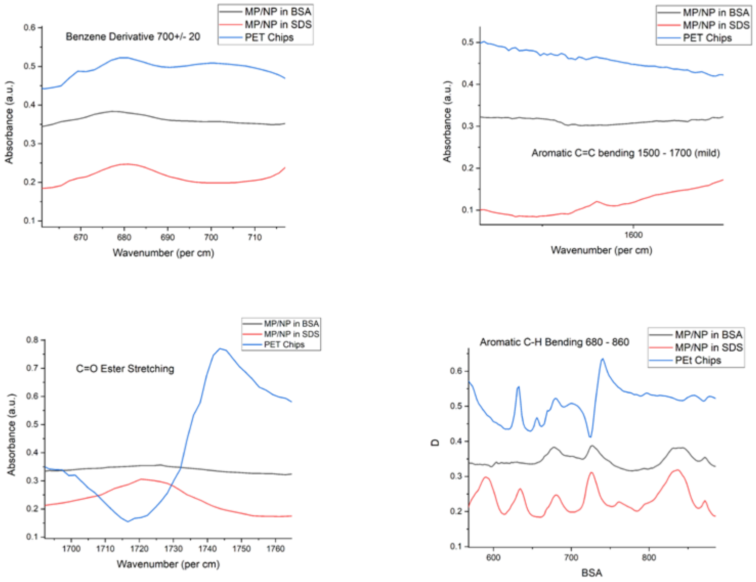


Fig. FTIR Peak Verification of PET chips and Micro/nano Size particles

Our results, as indicated in figure, show no change in the chemical composition of the MP/NP preparation. The characteristic peaks are coincident, with two suspensions of the MP/NP sample, one in BSA and the other in SDS. The BSA suspension shows a broader curve associated with the peaks – this is due to amino acid carbonyl vibrations arising close to the region of characteristic peaks. In SDS, however, extensive hydrogen bonding serves as a dampener to many inelastic vibrations, sharpening the graph.

Dynamic Light Scattering

Dynamic light scattering experiments were performed to measure the size range MP/NP colloidal suspension. The fragments obtained from the supernatant are found to be in the 80-90 nm range (nanoplastic particles) and in the 1000nm-1100nm range (microplastic particles). The resuspended pellet shows fragment sizes 5-6nm, 150-250 nm (NP), and 1050-1100nm (MP). These results are in good agreement with in vitro nanoplastic particles prepared with TFA digestion, as performed earlier in the field.[7]

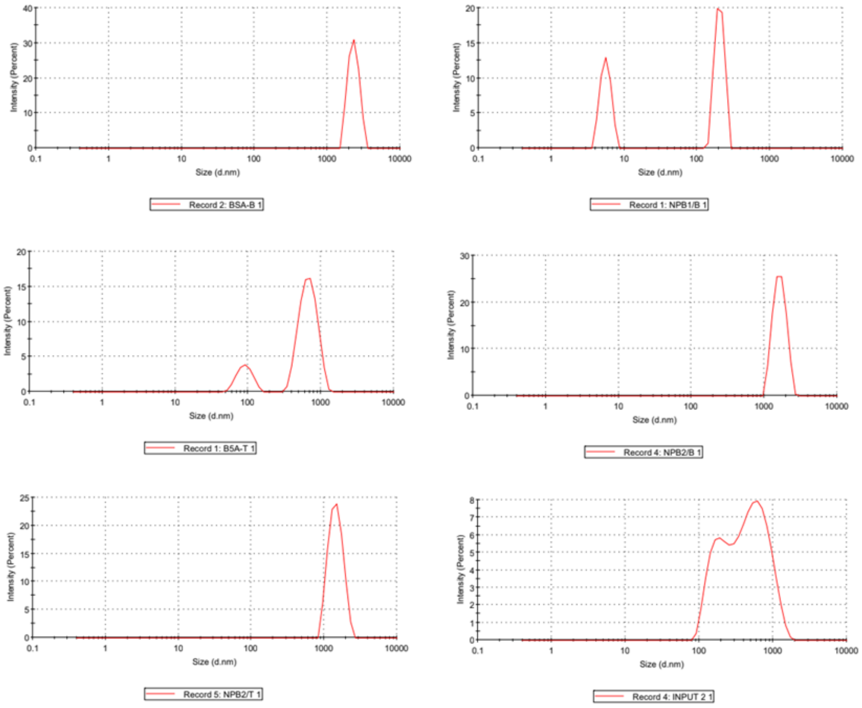


Fig. Dynamic Light Scattering of Different MP/NP batches

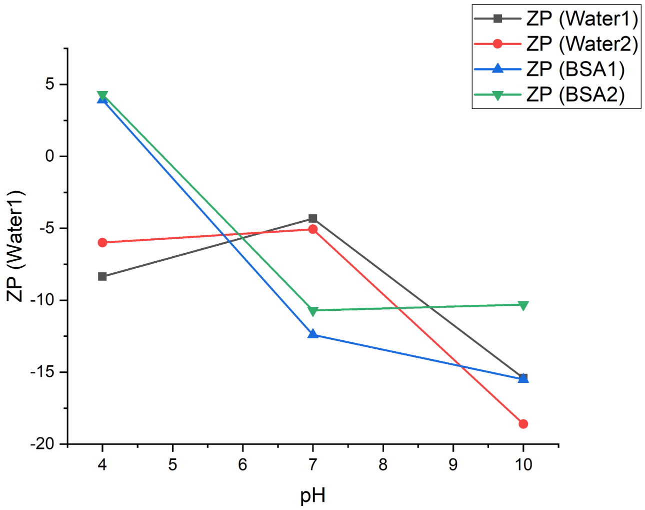


Fig. Zeta Potential of MP/NP suspended in BSA and water separately at different pH

SEM imaging of MP/NP preparation

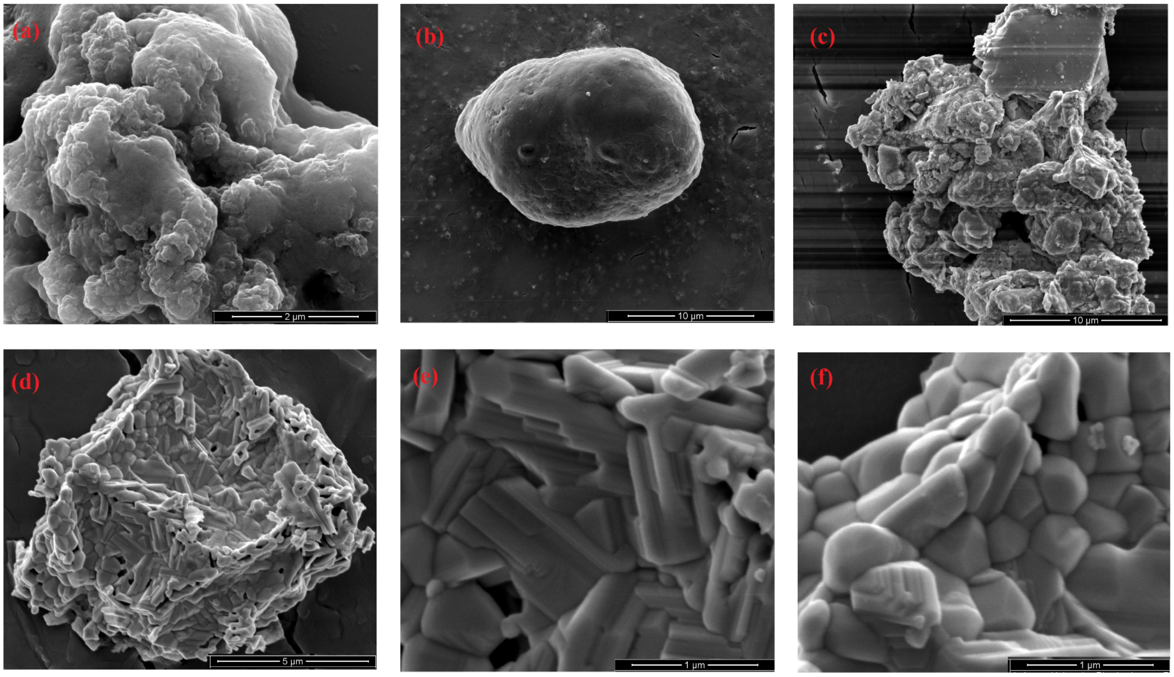


Fig. SEM images of PET micro and Nanoplastics at given scale discrete as well as agglomerated nanosized PET Plastics are clearly visible.

Nile Red Staining of *MP/NP*

nanoparticles were labeled with Nile red as a simple methodology proposed for plastic microparticle identification. One aliquot of NanoPET (1 mg mL−1) was centrifuged for 25 min at 16 800g and the supernatant was discharged. Then, 1 mL of Nile red solution (0.5% in dimethylsulfoxide) was added to the NanoPET pellet. The mixture was incubated at room temperature and gently stirred at 200 rpm for 24 hours in the dark. Then, the sample was washed three times by centrifugation with 50% ethanol in 0.1 M saline phosphate buffer (PBS 1×), pH 7.4. Prior to cell culture, fluorescent NanoPET was resuspended in complete Dulbecco's modified Eagle's medium (DMEM) containing an antibiotic and an antimycotic (penicillin/amphotericin B and streptomycin) and 10% fetal bovine serum (FBS). [22][7]

Macrophage Penetration by Nile Red-Tagged MP/NP :

Macrophage RAW-Blue cells (cells derived from the murine RAW 264.7) (InvivoGen) were cultured and maintained in DMEM containing 10% FBS + 1% penicillin/amphotericin B and streptomycin (Sigma-Aldrich). Subcultured cells among 8–12 passages at 80% confluence were used for cell–NanoPET experiments.

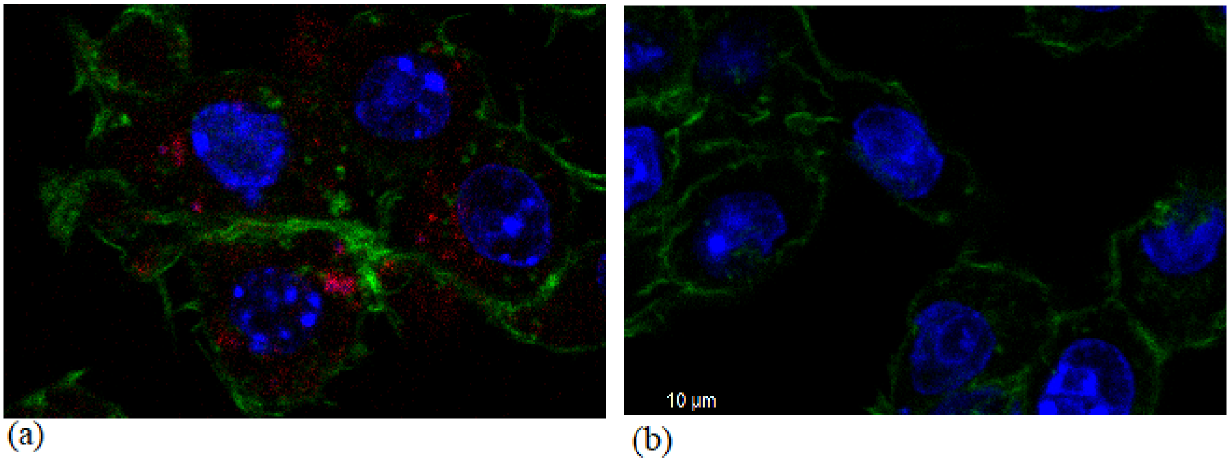


Fig. Nanoplastic Uptake (a) in RAW cell line along with the control (b).

MP/NP Accumulation in Brine Shrimp :

Artemia cysts were hatched at 30 parts per thousand salt concentration. 5 ml nile red tagged MP/NP were mixed at each hatching chamber. Air circulation through an air pump is carried out. Cysts were collected every 10-12 hours and fixed on slide for fluorescence microscope characterization.

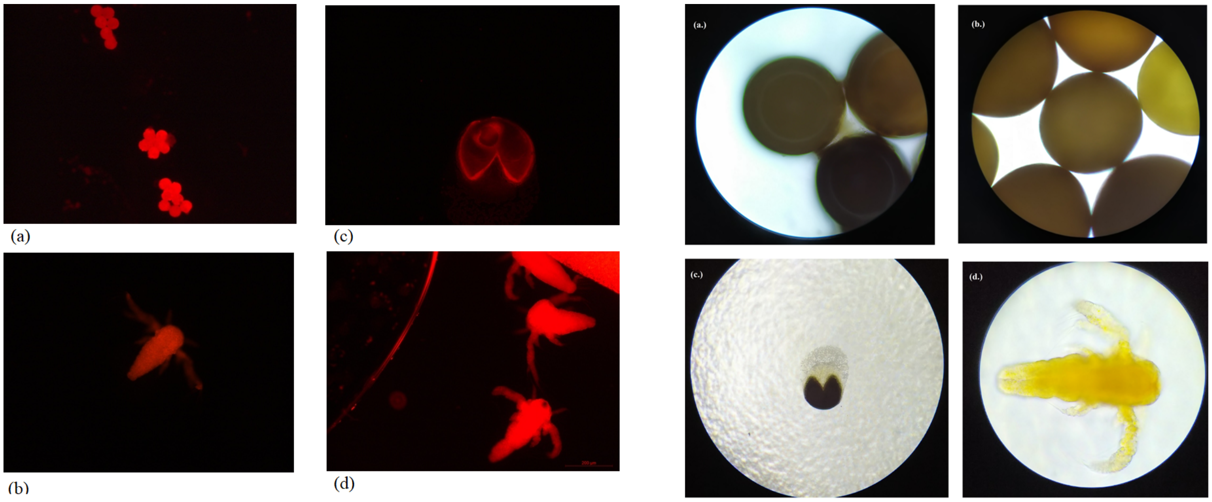


Fig. Microscopic image of Brine Shrimp at different points of its life cycle (Four pictures on right side). PET MP/NP accumulation in brine shrimp (Four images on the left). Nile red is glowing under the Red filter.

Synthesis of Ni-Fe Layered Double Hydroxide Crystals

Layer double hydroxides are two dimensional layered nanomaterials, belonging to the anionic clay family. The general formula of LDH is as follows: $[M_{1-X}{}^{2+} M_X{}^{3+} (OH)_2]^{X+} (A_{1-n})^{X-}]_n.\mathrm{m}H2\mathrm{O}$, where $M2+$ and $M3+$ represents metal cations having valences of 2 and 3 respectively, such as $Mg^{2+}$and Al^{3+}in the layers of the LDH. A^{n-} is representative of the interlayer anion, x is the molar ratio of $[M^{2+}]/[M^{3+}]$ and m stands for the number of water molecules between the laminates. LDHs occur in nature as the by-products of some metabolic activities of certain bacteria, as minerals, and also in some man-made context i.e., results of corrosion of some metal objects.

One of the simplest and most popular ways to make LDH is by co-precipitation. By adding bases such as aqueous NAOH and KOH, LDH is created using this approach from an aqueous solution that contains both the bivalent and trivalent metal cations of interest. Initially, in the right proportions, aqueous solutions of both divalent and trivalent metal ions are taken into a reactor. The co-precipitation of both metal ions from the aqueous solution is accomplished by simultaneously adding base at controlled temperature while vigorously mixing. Based on the nature of the metal ions, the pH of the reaction medium is maintained constant within the range of 7 to 10.[13]

Nickel Nitrate Hexahydrate and Ferric Nitrate Nonahydrate were coprecipitated in a flask with slow addition of NaOH and Na_2CO_3 under nitrogen environment until the at pH reaches 9.5. It is kept under constant stirring for 24 hours, followed by washing and centrifugation and drying to produce crystals of Ni-Fe LDH material. In order to test whether crystal formation was indeed successful, XRD was performed on the crystal and the results agreed with previous data in the field. These were further substantiated by SEM images of Ni-Fe LDH.

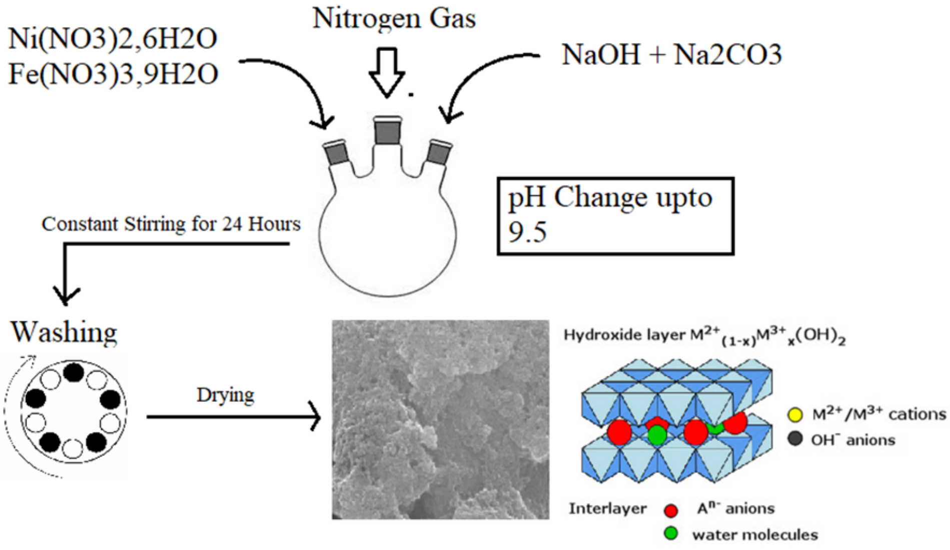


Fig. LDH Synthesis Process.

Having confirmed the crystalline nature of the LDH sample, we supplemented the results with SEM images of the LDH sample. Individual crystals are not visible because LDH has a strong and well documented propensity for agglomeration. Nevertheless, sharp edges are visible at the agglomerated ends – a feature of crystalline solids. Reduction of agglomeration was done with ultrasonication, but other techniques such as exfoliation could also be applied.

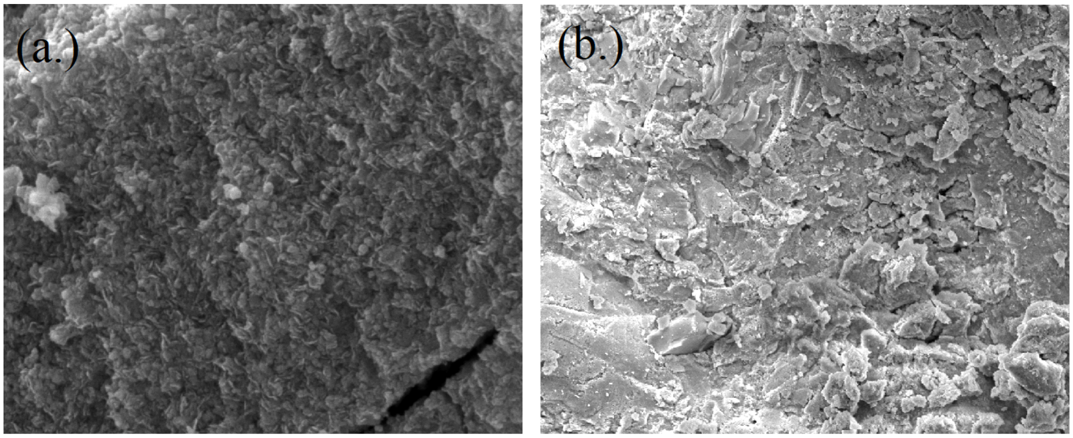


Fig. SEM Images of Ni-Fe LDH

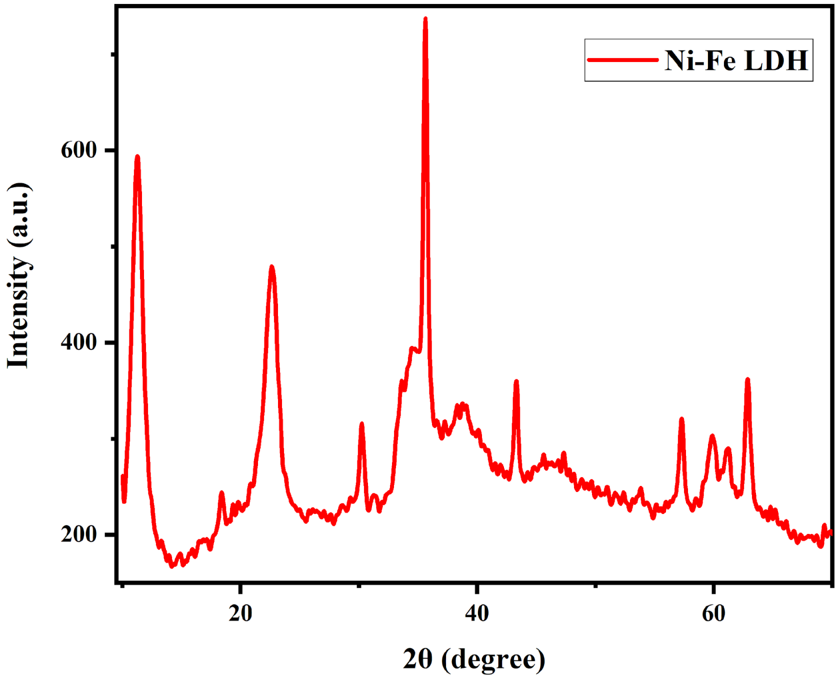


Fig. XRD of Ni-Fe Hydrotalcite. The diffraction peaks matched those reported in the reference data (ICDD card no. 01-082-8040). The reflections peaks at 11.6°, 23.2°, 34.5°, 39.1°, 46.5°, 59.9°, and 60.9° could be indexed to the plane families (003), (006), (012), (015), (018), (110), and (0015) respectively. The samples possessed a Rhombohedral crystal system with R-3 space *group (group number 148). The (003) interlayer distance was calculated to be (7.82Å) for the Ni/Fe LDH which is close to the literature value. [22]*

Synthesis of LDH-PSF membrane

For the manufacture of membranes, phase inversion is a popular process. This is a method of converting liquid-phase membranes to solid-phase membranes in a controlled manner. Precipitation from the vapor phase, controlled evaporation, thermal phase separation, or immersion precipitation are all methods for achieving phase inversion membranes. Immersion precipitation is a common technique that involves dissolving a polymer or polymer mixture in a suitable solvent and then casting it on a support layer. After that, the sample is immersed in a coagulation bath containing a separate solvent. Solvent exchange causes precipitation to occur.

Nanomaterials (NMs) can also be generated in situ during the casting process in the presence of the solvent. Pore size and distribution are affected by the presence of NMs. The size, loading, and kind of NMs, as well as how they interact with the polymer, determine the membrane's performance. NMs, depending on their type, can increase membrane qualities such as hydrophilicity, anti-fouling, and antimicrobial activity.

5g of PSF beads was dissolved in NMP (N-Methyl-2-pyrrolidone) solution. NI-Fe LDH was also added to the same solution and put on continuous stirring for overnight at 400 rpm. Finally, the completely dissolved casting solution was kept at room temperature for 12 h for degassing. The obtained homogenous solution was then cast on a dry glass by a film applicator. Immediately, the cast films were submerged in a water bath at 25 ± 2 °C. After 10 min, the resulting membranes were transferred to a freshwater bath and stored in water.

Diphenyl ether moieties crosslinked with sulfoxide moieties constitute the polysulfonate polymer used to constitute the membrane. This polysulfonate material is highly soluble in N-methyl pyrrolidone. Upon addition of Ni-Fe LDH crystals like powder sprinkled over the surface of this solution, and followed by phase inversion with water, a leathery membrane is formed due to coaggregation of the LDH crystals with the PSF polymer. This membrane was studied via SEM of cross-section. [14]

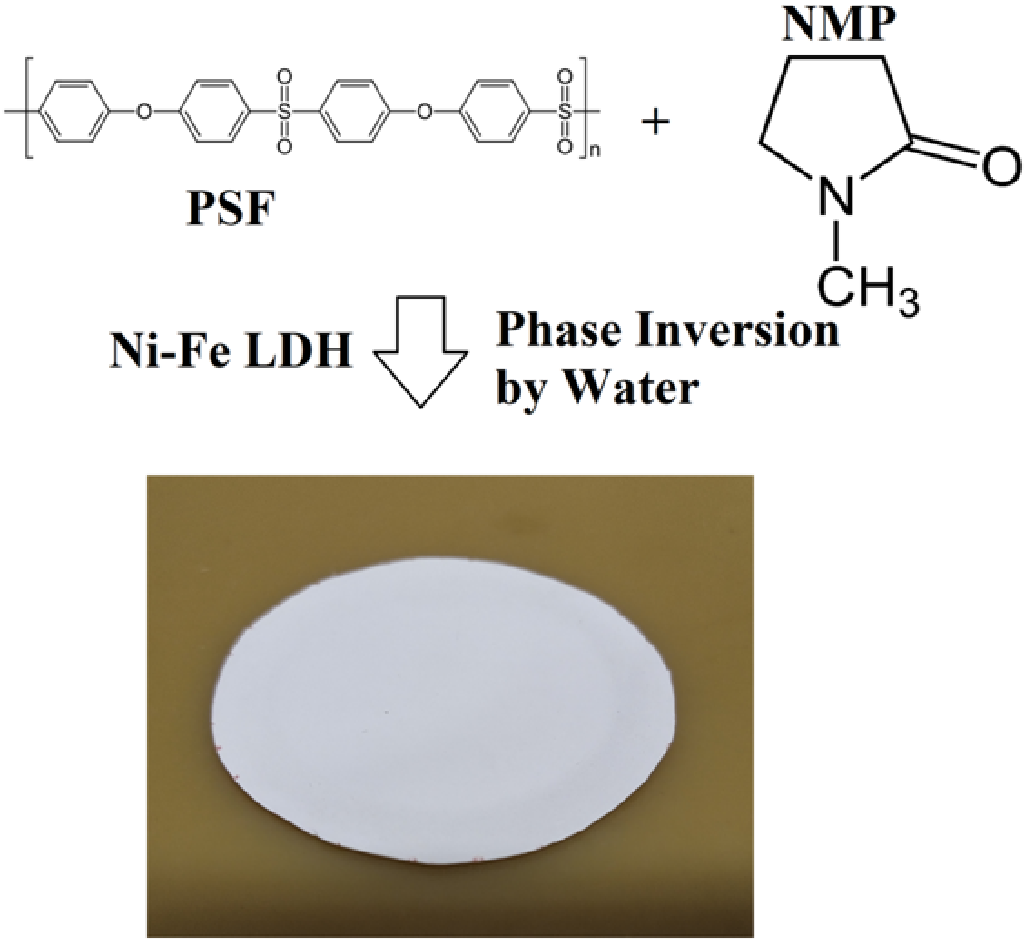


Fig. Membrane Fabrication by Phase Inversion Method

Filtration Efficacy Testing using PSF-LDH membrane with nanoparticles

Potential application of PSF-LDH membrane with nanoplastic particles is in removing suspended microplastic and nanoplastic particles from drinking water. Change in the UV-VIS absorbance profile of the input suspension and the filtrate was observed. The results were confirmed by Dynamic Light Scattering data from input suspension of microplastic and nanoplastic particles and output suspension, which showed exclusion of particles corroborated by absorbance data.

Results, Figures and Discussion

This crystalline form of the sample was then used to create the filter membrane. We have used Polysulfone (PSF) as polymer and N-Methyl-2- Pyrrolidone (NMP) as solvent. First , we have dispersed LDH nanoparticles into the solvent through sonication for 30 mins ,then the polysulfone homopolymer is added into the solution. Then the mixture is casted on a support layer. Then, it is submerged into a coagulation bath containing the non solvent phase. In this case the non solvent phase is water. Due to solvent and nonsolvent phase exchange, nonequilibrium phase dynamics is set up, causing precipitation. The combination of mass transfer and phase separation affects the membrane structure. The presence of LDH nanoparticles in the membrane affects the pore size and distribution. This is shown in the figure.

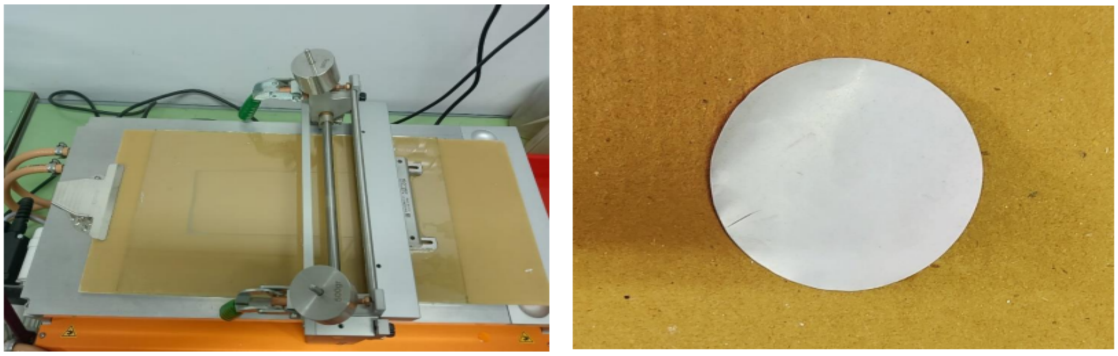
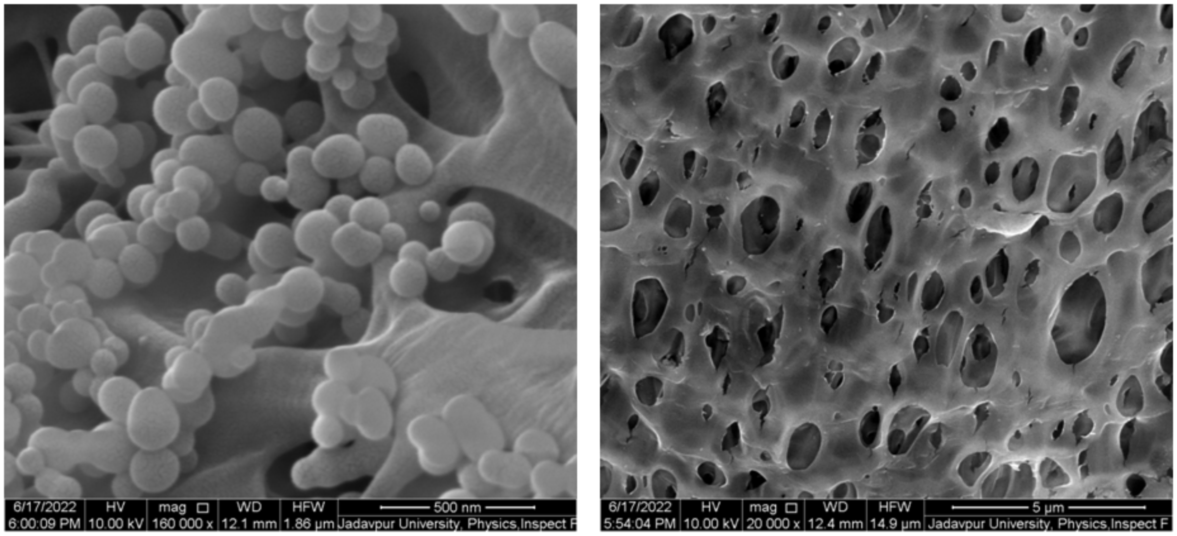


Fig. Membrane Fabrication Machine (left) and the PSF Membrane (right)

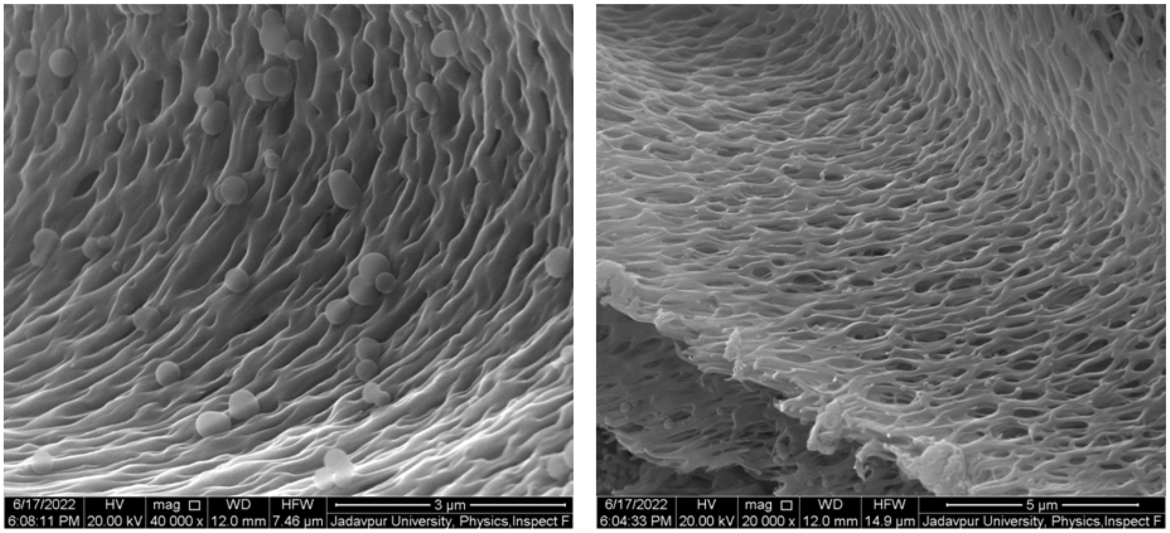
SEM imaging of the PSF-LDH membrane in association with MP/NP particles and control

LDH membranes have been shown in recent work to be highly useful tools in bioengineering, particularly in studies monitoring cell adhesion properties and cell sorting experiments, a feature arising out of the unique microenvironment it offers and the potential kinetic and thermodynamic advantages thereof.[21]

SEM of the edge of the membrane (cross Section)



Here the membrane channels are shown with associated LDH Nanoparticles.



Here the membrane pores are clearly visible, varying in size, the largest among them (bottom right) being around 1 micrometer in diameter.

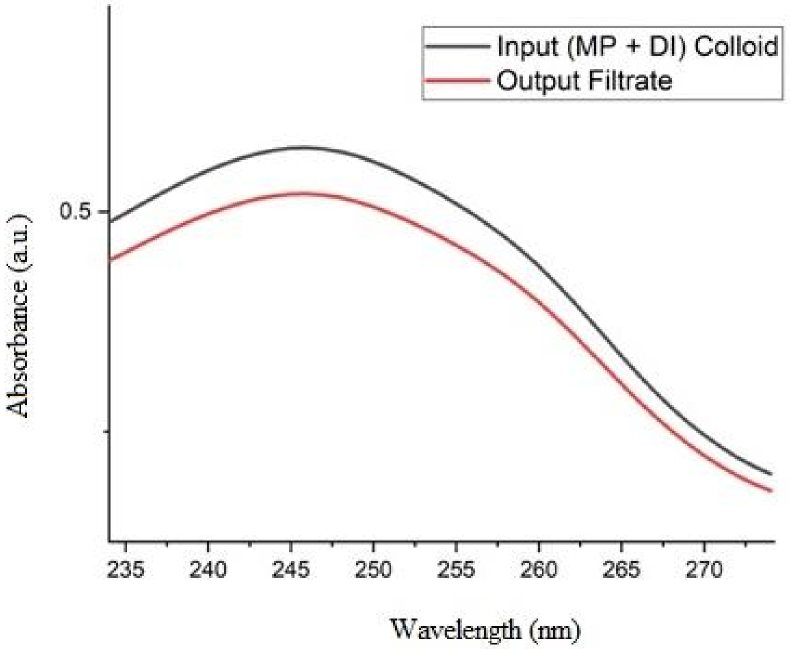
In contrast, if we see the SEM images for the membrane without treatment with MP/NP suspension, we notice the fine ultrastructure of the membrane.

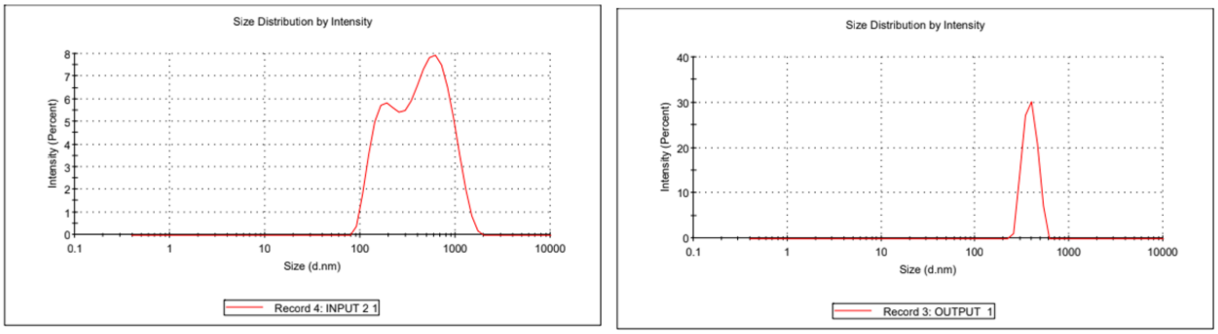
These membranes were then subjected to the filtration assay.[22] And the results of filtration were observed under UV-VIS spectrophotometer for absorbance profiles. Two points must be made here – firstly, the absorbance profile of the spectrum remained the same, indicating that no chemical reaction was occurring, as the signature of absorbance of all molecules in the suspension pre-filtration were retained in the filtrate. Secondly, the drop in absorbance has to do with a population issue – the population of absorbing molecules in the filtrate is lesser than the pre-filtrate. This indicates a non-specific physical filtration process that operates on non-covalent interactions such as size exclusion, hydrogen bonding, van der Waals interactions, hydrophobic interactions and aromatic stacking as the predominant forces making up the interaction between the membrane polymer molecules and the suspension.

From a physicochemical point of view it is evident that the treated PSF-LDH membrane should be more effective at filtration than the Only-PSF membrane.

UV-VIS and DLS experiments on the filtrate

MP/NP removal by PSF-LDH membrane. UV-Vis spectroscopy reveals that there has been a significant density decrease of the suspension.





Input Solution

Output Solution

Fig. Filtration Efficiency of PSf Membrane. It Clearl;y shows reduction of higher size range particles.

Conclusion

The work done in this paper was according to the guidelines of several disparate works by other workers in the field, however, the novel usage of TCA for digestion, and the usage of PSF-LDH membrane for filtration of microplastics and nanoplastics in suspension may be a novel step forward in designing a filtration protocol designed to eliminate these noxious bioaccumulating molecules from drinking water. The potential applications of the work extend to as diverse areas as agriculture and public health. We conclude on a warning note about the serious health hazard posed by microplastics and nanoplastics to marine life, particularly when biomagnified through trophic levels and reaching potentially catastrophic human impact.

References

1. H. Ritchie and M. Roser (2018) - *"Plastic Pollution". Published online at OurWorldInData.org*. Retrieved from: ' https://ourworldindata.org/plastic-pollution '
2. J.P. da Costa, et al., *(Nano)plastics in the environment - Sources, fates and effects*. Sci. Total Environ., 2016, 566-567, 15-26.
3. R.C.P. Monteiro, J.A. Ivar and M.F. Costa, *Plastic pollution in islands of the Atlantic Ocean.* Environ. Pollut., 2018, 238, 103-110.
4. F. Bessa, et al., *Occurrence of microplastics in commercial fish from a natural estuarine environment.* Marine Pollut. Bull., 2018, 128, 575-584.
5. J.F. Provencher, et al., *Garbage in guano? Microplastic debris found in fecal precursors of seabirds known to ingest plastics.* Sci. Total Environ., 2018, 644, 1477-1484.
6. D. Magrì, et al., *Laser ablation as a versatile tool to mimic polyethylene terephthalate nanoplastic pollutants: characterization and toxicology assessment.* ACS Nano, 2018, 12, 7690-7700.
7. Rodriguez-Hernandez A.G. et al. *A Simple method for polyethylene terephthalate nanoparticle production*, Environ. Sci.: Nano, 2019, 6, 2031-2036
8. Tzourou, P. et al. *Measuring the Size and the Charge of Microplastics in Aqueous Suspensions With and Without Microorganisms Using a Zeta-Sizer Meter: Proceedings of the 2nd International Conference on Microplastic Pollution in the Mediterranean Sea,* 2020
9. I. Donelli, et. al, *Enzymatic Surface modification and functionalization of PET: a water contact angle, FTIR, and fluorescence spectroscopy study*. Biotechnol. Bioeng., 2009, 103, 845-856.

10. F. Caputo, et al. *Measuring particle size distribution and mass concentration of nanoplastics and microplastics: addressing some analytical challenges in the sub-micron size range,*
Journal of Colloid and Interface Science, Volume 588, 2021, 401-417.

11. Comeche, A., et. al., 2017. *Effect of methylparaben in Artemia franciscana*. Comp. Biochem. Physiol. Part - C Toxicol. Pharmacol. 199, 98–105. https://doi.org/10.1016/j.cbpc.2017.04.004.
12. T. Maes, et. al, *A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red*. Sci. Rep., 2017, 7, 44501.
13. Daniel, S., & Thomas, S. (2020). Layered double hydroxides: fundamentals to applications. In Layered Double Hydroxide Polymer Nanocomposites (pp. 1–76). Elsevier. https://doi.org/10.1016/b978-0-08-101903-0.00001-5
14. E. Lufrano, et al. Barrier properties of sulfonated polysulfone/layered double hydroxides nanocomposite membrane for direct methanol fuel cell operating at high methanol concentrations, International Journal of Hydrogen Energy, Volume 45, Issue 40, 2020, Pages 20647-20658, https://doi.org/10.1016/j.ijhydene.2020.02.101
15. Sebastian Primpke, Matthias Godejohann, and Gunnar Gerdts, *Rapid Identification and Quantification of Microplastics in the Environment by Quantum Cascade Laser-Based Hyperspectral Infrared Chemical Imaging*, Environmental Science & Technology 2020 54 (24), 15893-15903 DOI: 10.1021/acs.est.0c05722
16. Ahmad, Atta & Madhusudanan, Kunnath & Bhakuni, Vinod. (2000). *Trichloroacetic acid and trifluoroacetic acid-induced unfolding of cytochrome c: Stabilization of a native-like folded intermediate*. Biochimica et Biophysica Acta (BBA) - Protein Structure and Molecular Enzymology. 1480. 201-210. 10.1016/S0167-4838(00)00069-8.
17. Immobilization of silver nanoparticles on polyethylene terephthalate - Scientific Figure on ResearchGate. Available from: https://www.researchgate.net/figure/Zeta-potential-Zeta-potential-determined-on-pristine-PET-PET-treated-by-plasma_fig5_263705546
18. Gniadek, Marianna; Dąbrowska, Agnieszka (2019). *The marine nano- and microplastics characterisation by SEM-EDX: The potential of the method in comparison with various physical and chemical approaches.* Marine Pollution Bulletin, 148(), 210–216. doi:10.1016/j.marpolbul.2019.07.067
19. Johari, S.A. et al., 2018. *Introducing a new standardized nanomaterial environmental toxicity screening testing procedure, ISO/TS 20787: aquatic toxicity assessment of*

manufactured nanomaterials in saltwater lakes using Artemia sp. nauplii. Toxicol. Mech. Methods https://doi.org/10.1080/15376516.2018.1512695

20. 20. Wang, N., et al. (2020). *Vacuum-assisted assembly of iron cage intercalated layered double hydroxide composite membrane for water purification*. In Journal of Membrane Science (Vol. 603, p. 118032). Elsevier BV.
https://doi.org/10.1016/j.memsci.2020.118032
r21. Arrabito, G. et al. (2019). *Layered Double Hydroxides: A Toolbox for Chemistry and Biology*. Crystals. 10.3390/cryst9070361.

21. 22. Cigdem B. et al., *Fabrication of PSf nanocomposite membranes incorporated with ZnFe layered double hydroxide for separation and antifouling aspects,*Separation and Purification Technology, Volume 285, 2022, 120354, ISSN 1383-5866, https://doi.org/10.1016/j.seppur.2021.120354

22. Basu, Debdipta, et al. "Advances in layered double hydroxide (LDH)-based elastomer composites." *Progress in Polymer Science* 39.3 (2014): 594-626.

23. Maes, Thomas, et al. "A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red." *Scientific reports* 7.1 (2017): 1-10.