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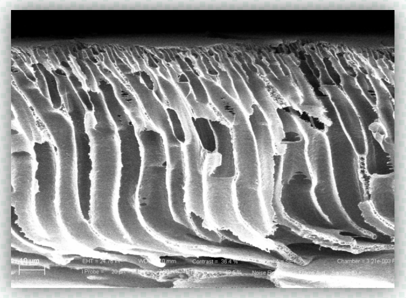
Mitigation measure : state of the art



A. Figoli, F. Russo

Institute on Membrane Technology (ITM-CNR), Via P. Bucci 17/c Rende (CS), Italy

a.figoli@itm.cnr.it

16 September
14:00 - 15:30 Environmental Nanotechnologies: the issue of micro-nanoplastics - Impact and mitigation measures of micro and nanoplastics WS.III.1 - TT.III.D

NANOINNOVATION 2020

Consiglio Nazionale delle Ricerche

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The microplastics in the marine environments

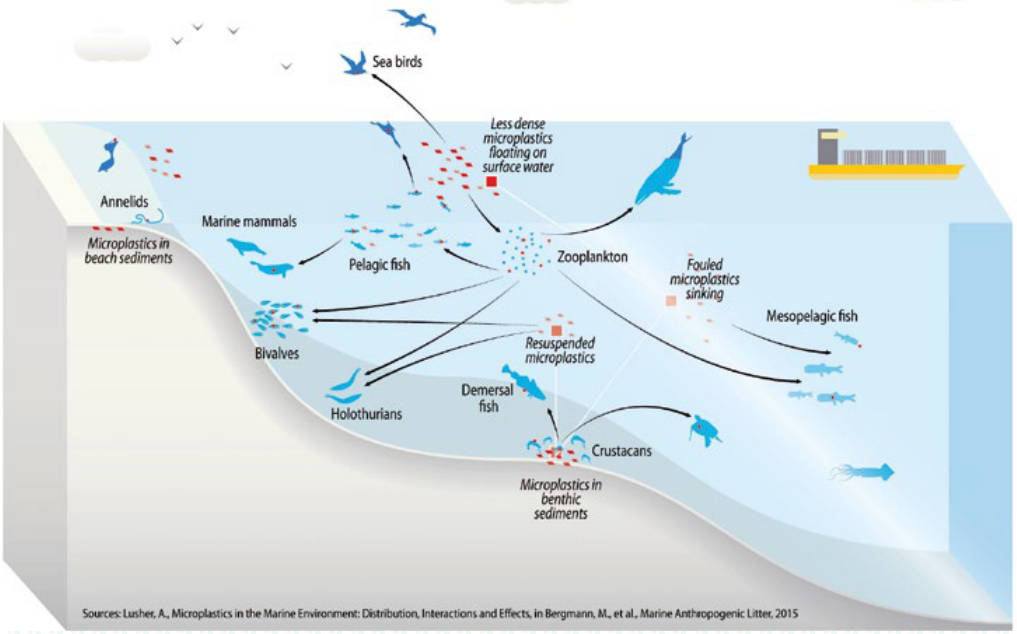
Microplastics are microscopic sized plastics having less than 5mm in diameter, according to the National Oceanic and Atmospheric Administration (NOAA), from the production of personal care products and fragments of larger plastics (eg. degradation of bottles, food rappers, plastic bags etc.). *

The largest producer of plastics:

- ✓ Asia 50.1 %
- ✓ Europe 18.5 %
- ✓ North American 17.7 %
- ✓ Middle East, Africa 7.71 %
- ✓ Latin America 4 %
- ✓ Commonwealth of Independent States 2.6 %

Pathways for microplastics

In the marine environment, plastics undergo a process of weathering and fragmentation that breaks down macrodebris into smaller micro- and nanodebris. (**)



Microplastic it self can move across the food chain and pose significant public health issues to society.

*NationalOceanService,2017
**https://www.grida.no/resources/6904; microplastiche e possibili effetti sull'uomo, ECOSCIENZA Numero 1 • Anno 2020.

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The microplastics in the marine environments

The Mediterranean Sea is today one of the seas with the highest levels of plastic pollution in the world. According to the report "Out of the Plastic Trap: Saving the Mediterranean from plastic pollution", published by WWF in June 2018, plastics account for 95% of the waste in the open sea, on the seabed and on beaches across the Mediterranean.

* https://medwet.org/2019/05/world-migratory-bird-day-2019-plastic/

The microplastics in the marine environments

Effects of microplastics

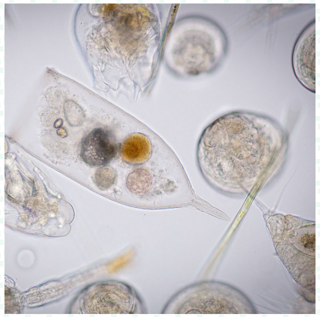
A major problem with microplastic material is their ability to adsorb other common environmental contaminants, such as metals, pharmaceuticals, personal care products and others

Consequently, the microplastic can potentially cause diseases such as cancer, a malformation in animals and humans, impaired reproductive activity, and reduced immune response.

Effects of microplastics on man

Potential risk:

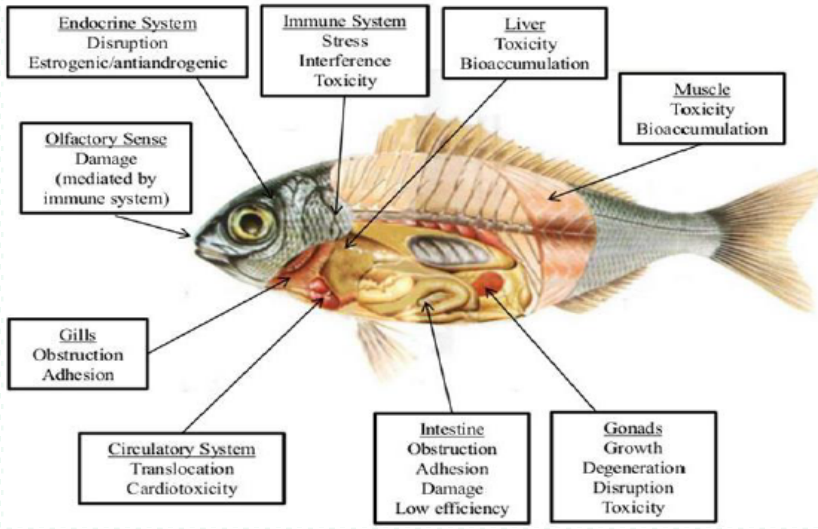
- to food insecurity



- and in body systems such as digestive, reproductive and respiratory.

Effects of microplastics on marine organisms

The effects of plastic debris on marine organisms as a result of ingestion include: •gut blockages; •heightened immune response;
- reproductive processes; •other.



*https://www.barillacfn.com/it/magazine/cibo-e-sostenibilita/aiuto-c-e-una-microplastica-nel-mio-piatto/

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The microplastics in the marine environments

MACROPLASTICS
≥25mm

MESOPLASTICS
<25 - 5mm

MICROPLASTICS (MP)
<5 - 1mm

NANOPLASTICS (MP)
<1mm*

Plastic pollution size

* Revisited by the author.

Type of microplastics (MP)

PRIMARY MICROPLASTICS

They include small pieces of specially manufactured plastic, such as hand and facial cleansers, shower gels, toothpaste, industrial scrubbers, and plastic micro-nanospheres, etc.

SECONDARY MICROPLASTICS

They include small pieces of plastic derived from the deterioration of larger plastic waste both at sea and on land.

Microplastics (MP) for European Chemical Agency (ECHA):

"a material consisting of solid polymer-containing particles, to which additives or other substances may have been added, and where ≥ 1% w/w of particles have (i) all dimensions 1nm ≤ x ≤ 5mm, or (ii), for fibres, a length of 3nm ≤ x ≤ 15mm and length to diameter ratio of >3."

*https://journals.openedition.org/
**https://www.nurdlehunt.org.uk/
***http://www.unoosa.org/documents/pdf/psa/activities/2018/PakistanConference/Presentations/7-FUNMILOLA_OLUWAFEMI_NASRDA-MICROPLASTICS_AS_ENVIRONMENTAL_STRESSOR_AND_THREAT_TO_HUMAN_AND_SEA_LIFE.pdf

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The microplastics in the marine environments

Microplastics materials

The fragmentation of plastic is caused by a combination of mechanical forces, for example waves and/or photochemical processes triggered by sunlight.

Plastics are usually synthesized from fossil fuels, but biomass can also be used as feedstock.

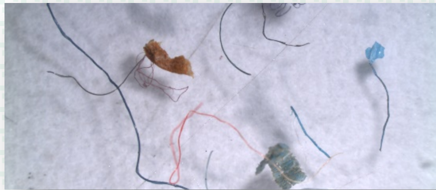
Most microplastics contain **organic polymers** with chains of carbon atoms:

- Polyethylene
- Polypropylene
- Polyethylene terephthalate
- Polymethyl methacrylate
- polyvinyl-chloride (PVC)
- polycarbonate (PC)
- polyamides (PA)
- Polyester (PES)

Some of microplastics are biodegradable and photodegradable by UV radiation, designed to fragment quickly into small particles.

Common Microplastics

Fibres
from clothing



- Non-Biodegradable

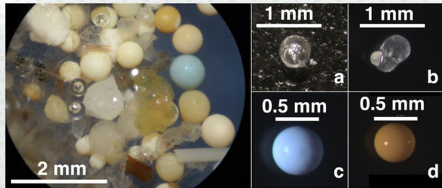
Fragments
from large plastics

- Degradable by UV Radiation

Foam
from food or coffee cups

Pellets
from manufacturing

Microbeads
From cosmetics and soaps



- Non-Biodegradable

*http://www.unoosa.org/documents/pdf/psa/activities/2018/PakistanConference/Presentations/7-FUNMILOLA_OLUWAFEMI_NASRDA-MICROPLASTICS_AS_ENVIRONMENTAL_STRESSOR_AND_THREAT_TO_HUMAN_AND_SEA_LIFE.pdf

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The microplastics in the marine environments

Microplastics materials

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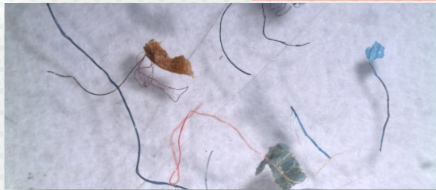
Frequency of occurrence of different polymer types in microplastic debris sampled at sea or in marine sediments:

Polymer type	Specific density*	% Studies (n)
Polyethylene (PE)	0.91–0.94	31 (33)
Polypropylene (PP)	0.90–0.92	25 (27)
Polystyrene (PS)		16 (17)
Polyamide (nylon) (PA)		6.0 (7)
Polyester (PES)		3.7 (4)
Acrylic (AC)		3.7 (4)
Polyoxymethylene (POM)		3.7 (4)
Polyvinyl alcohol (PVA)		2.8 (3)
Polyvinyl chloride (PVC)		1.8 (2)
Poly methylacrylate (PMA)		1.8 (2)
Polyethylene terephthalate (PET)		0.9 (1)
Alkyd (AKD)		0.9 (1)
Polyurethane (PU)		0.9 (1)

*Hidalgo-Ruz V, Gutow L, Thompson RC, Thiel M. Microplastics in the marine environment: a review of the methods used for identification and quantification. Environ Sci Technol. 2012;46:3060–3075.

Common Microplastics

Fibres
from clothing



- Non-Biodegradable

Pellets
from manufacturing

Fragments
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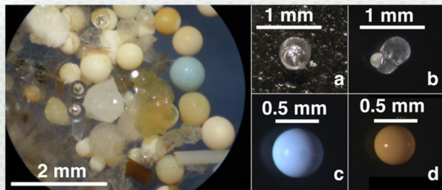
Microbeads
From cosmetics and soaps

Foam
from food or coffee cups



- Non-Biodegradable

PE and PP are the most frequency materials in microplastic debris, for their specific density that is less than of marine water (~1.02) and may be located on the surface.

The technologies for microplastics removal

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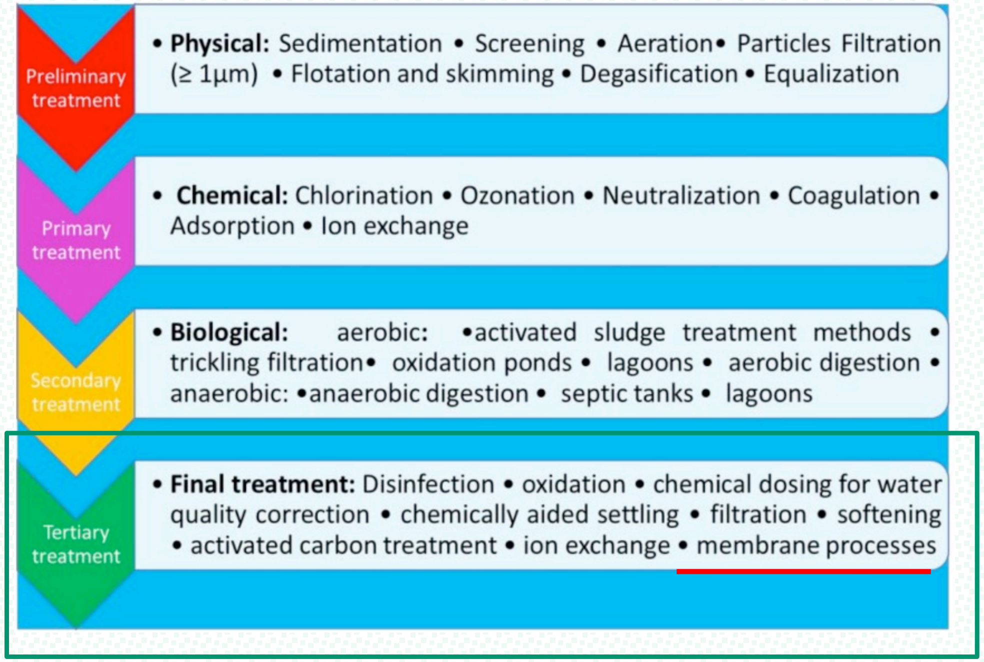
Microplastics Removal

The wastewater processing for plastic pollution can be grouped into four main treatments:

- ✓ preliminary treatment,
- ✓ primary treatment,
- ✓ secondary treatment,
- ✓ and tertiary treatment or advanced treatment.

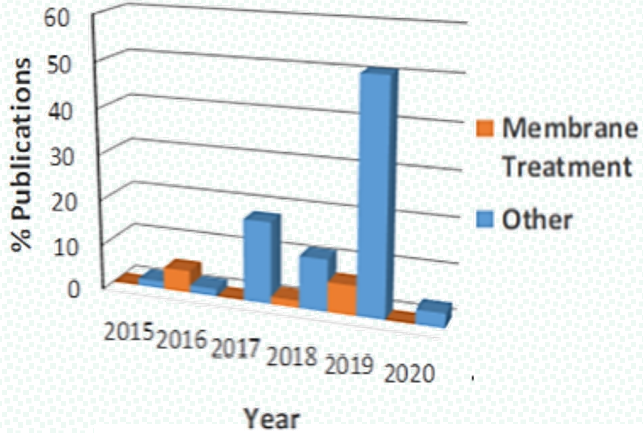


ADVANCED TECHNOLOGIES

The tertiary treatments included different filtering (sand and cloth), flotation techniques and membrane processes.

- ✓ Micro-screen filtration with discfilters (DF)
- ✓ Rapid (gravity) sand filters (RSF)
- ✓ Dissolved Air Flotation (DAF)
- ✓ Membrane bioreactor (MBR)

The distribution of publications related to microplastic contaminant removal from 2015 to 2020.



*T. Poerio, E. Piacentini, R. Mazzei, Membrane processes for microplastic removal, Molecules, 24 (2019), 4148.

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The technologies for microplastics removal

Microplastics Removal

ADVANCED TECHNOLOGIES

✓ Micro-screen filtration with discfilters (DF)

The process is based on primary clarification, conventional activated sludge (CAS) process and a tertiary denitrifying biological filter (BAF).

✓ Membrane bioreactor (MBR)

The MBR pilot included Submerged Membrane Unit (SMU) and ultrafiltration (UF) process. During the filtration, the water is forced through membranes under negative pressure created by pumps and collected to the separate tank. MBRs are the combination of membrane filtrations processes with suspended growth biological reactors. This combination treats primary effluent containing suspended solids as well as dissolved organic matter and nutrients. Hence the MBR technology replaces secondary clarifiers in CAS systems.

✓ Dissolved Air Flotation (DAF)

In DAF, water is saturated with air at high pressure and then pumped to a flotation tank at 1 atm, forming dispersed water. The released air bubbles in dispersed water adhere to the suspended solids causing them to float to the surface, from where it is removed by skimming. Before the flotation, flocculation chemical Polyaluminium Chloride (PAX) is added to the wastewater with dosage of 40 mg/L to enhance flocculation. Before the DAF, the process is based on CAS process.

✓ Rapid (gravity) sand filters (RSF)

In RSF, the wastewater is filtered through a layer of sand. The sand filter composed of 1 m of gravel with gain size of 3e5 mm and 0.5 m of quartz with grain size 0.1e0.5 mm. Apart from physical separation removing suspended solids, adhesion by microbes removes nutrients and microbes. Before the sand filter the process is based on CAS method.

* J. Talvitie, A. Mikola, A. Koistinen, O. Setälä, Solutions to microplastic pollution – Removal of microplastics from wastewater effluent with advanced wastewater treatment technologies, Water Res. 123 (2017) 401–407

The technologies for microplastics removal

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Microplastics Removal

ADVANCED TECHNOLOGIES

- ✓ Micro-screen filtration with discfilters (DF)
- ✓ Dissolved Air Flotation (DAF)
- ✓ Rapid (gravity) sand filters (RSF)
- ✓ Membrane bioreactor (MBR)

case study

The average microplastic concentrations before and after the treatments.

Treatment	Effluent type	Before (MP/L^{-1})	After (MP/L^{-1})	Removal (%)
DF 1	Secondary	0.5 (±0.2)	0.3 (±0.1)	40.0
DF 2	Secondary	2.0 (±1.3)	0.03 (±0.01)	98.5
RSF	Secondary	0.7 (±0.1)	0.02 (±0.007)	97.1
DAF	Secondary	2.0 (±0.07)	0.1 (±0.04)	95.0
MBR	Primary	6.9 (±1.0)	0.005 (±0.004)	99.9

DF10: discfilter with pore size 10 mm, DF 20: discfilter with pore size 20 mm, RSF: rapid sand filters, DAF: dissolved air flotation and MBR: membrane bioreactor.
Data is given in number of microplastics per liter of effluent

advantages of MBR:

1. With the MBR technology,MP concentration decreased from 6.9 (±1.0) to 0.005 (±0.004) MP L1. The MBR treats primary clarified wastewater with much higher MP concentration compared to secondary effluent, giving higher removal percentage than tertiary treatments.

2. MBR gave also the lowest MP concentration of the final effluent, which indicates, that MBR is the most efficient technology in this study to remove MPs from wastewater. The result is expected as the MBR filters had the smallest pore size (0.4 mm) of for all the studied filters.

* J. Talvitie, A. Mikola, A. Koistinen, O. Setälä, Solutions to microplastic pollution – Removal of microplastics from wastewater effluent with advanced wastewater treatment technologies, Water Res. 123 (2017) 401–407

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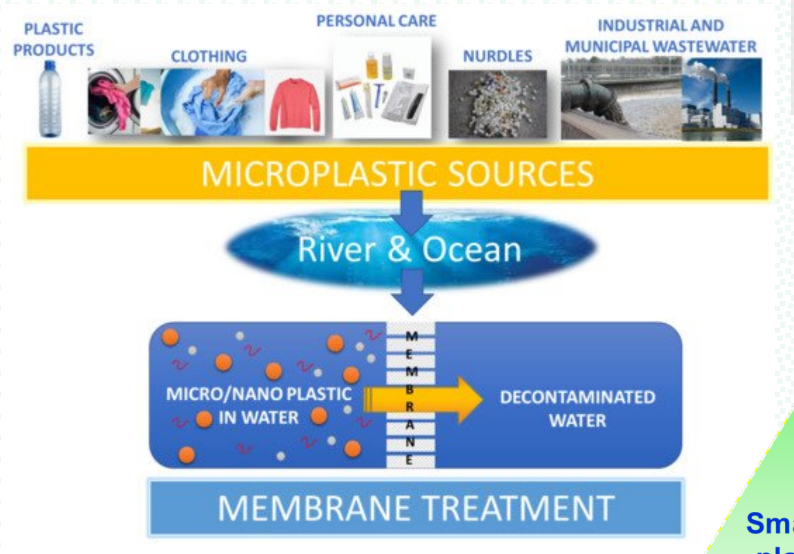
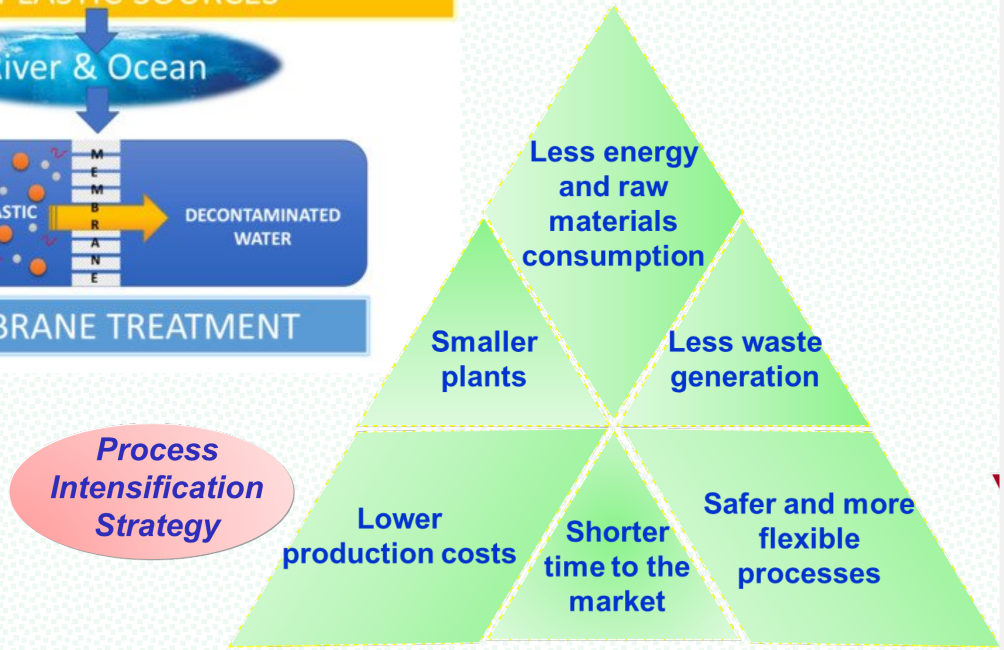
The membrane technology for microplastics removal

Microplastics Removal

Membrane technology (MT) for MP removal



MT can be **considered as one of the Best Available Technologies (BAT)*** by the European Commission.



In the wake of Process Intensification strategy and the 17 Sustainable Development Goals guidelines, Membrane Science can be identified as a green technology that offers a lot of advantages[2] such as:

1. the possibility of integration with conventional technologies,
2. Low cost,
3. Low energy requirement,
4. safety and flexible scaling up,
5. Good stability and compatibility,
6. High selectivity and permeability for the transport of components,
7. Environment-compatibility.

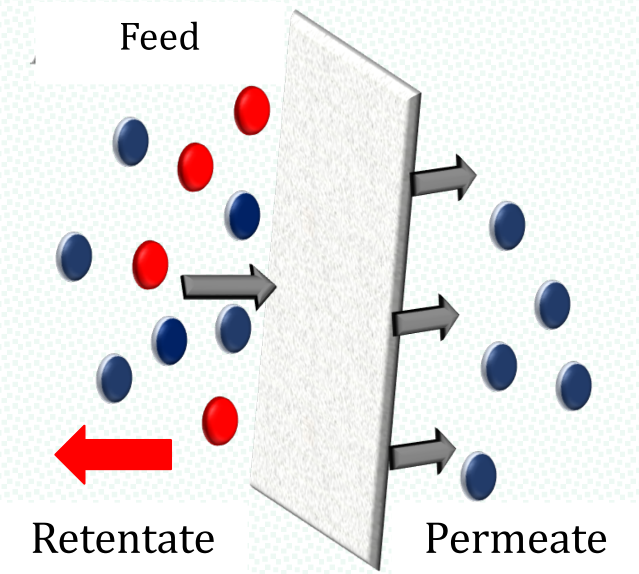
*T. Poerio, E. Piacentini, R. Mazzei, Membrane processes for microplastic removal, Molecules, 24 (2019), 4148.

The membrane technology for microplastics removal

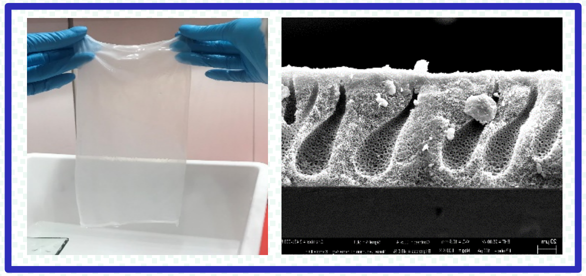
Microplastics Removal

What is a membrane?

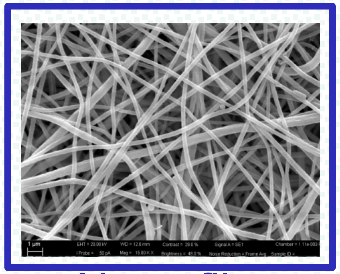
A membrane can be defined as a selective active barrier for particles transport between two adjacent phases regulating by the specific particle sizes and the molecular weights of the components.



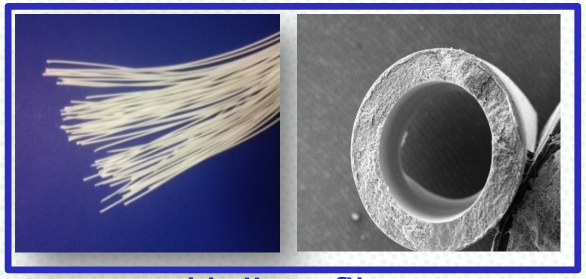
Membrane types:



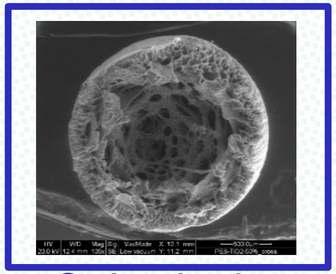
Flat sheet



Nano-fiber



Hollow fiber



Spherical

* Figoli et al., Polymeric Membranes, Chapter 1, pp 1-44, In Membrane Fabrication, Edited by Nidal Hilal, Ahmad Fauzi Ismail, and Chris Wright, CRC Press, Print ISBN: 978-1-4822-1045-3; 2015

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The membrane technology for microplastics removal

Membrane materials

Classification:

Morphology[1]

Asymetric or anisotropic

Composite
(with skin 0.1-0-5 μm)

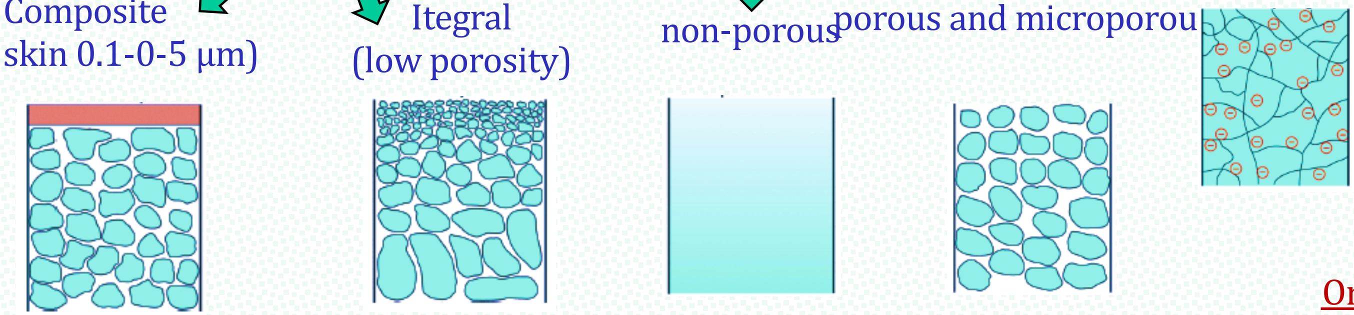
Itegral
(low porosity)

Symetric or isotropic

non-porous

porous and microporou

ion-exchange



State

amorphous

semicrystalline

crystalline

Origin

natural

organic
(bio-polymers)

inorganic

artificial

organic
(polymeric)

rubbery

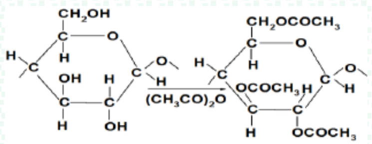
glassy

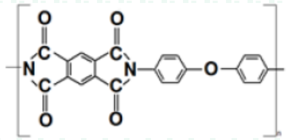
* Figoli et al., Polymeric Membranes, Chapter 1, pp 1-44, In membrane fabrication, Edited by Nidal Hilal, Ahmad Fauzi Ismail, and Chris Wright, CRC Press, Print ISBN: 978-1-4822-1045-3; 2015.
** Lee et al., Membrane materials for water purification: design, development, and application, Environ. Sci.: Water Res. Technol., 2016, 2, 17.
*** Strathmann et al., Fundamentals, Chapter 2, pp. 22-23., in An Introduction to Membrane Science and Technology, CONSIGLIO NAZIONALE DELLE RICERCHE, Roma, 2006.

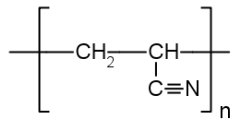
The membrane technology for microplastics removal

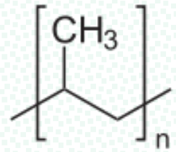
Membrane materials

Polymers:

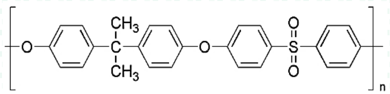

Cellulose acetate

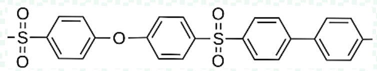

Polyimide

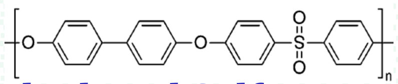

Polyacrylonitrile


Polypropilene

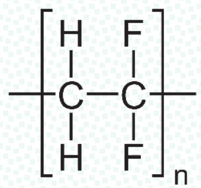
Sulfone-based polymers


Polysulfone


Polyether Sulfone

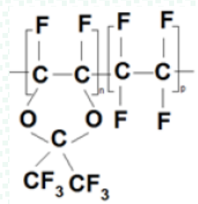

Polyphenyl Sulfone

Fluoropolymers



High Performance in term of chemical and mechanical stability.

Polyvinylidene difluoride (PVDF)


Teflon

Good electrical properties
Good chemical resistance
Stable over a wide range of temperatures
High temperature resistance

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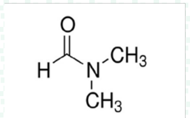
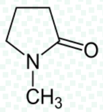
The membrane technology for microplastics removal

Membrane materials

Solvents:



DMF



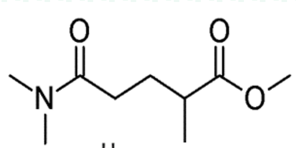
NMP

DMA

Traditional toxic solvents in membrane preparation

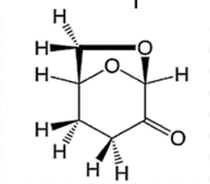
The use of renewable solvents derived from biomass is of great interest for producing membrane in a more sustainable way, according to Green Chemistry design.

Bio-based solvents



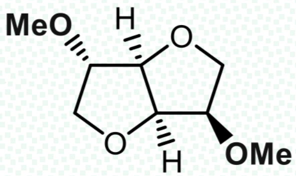
POLARCLEAN®

methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate

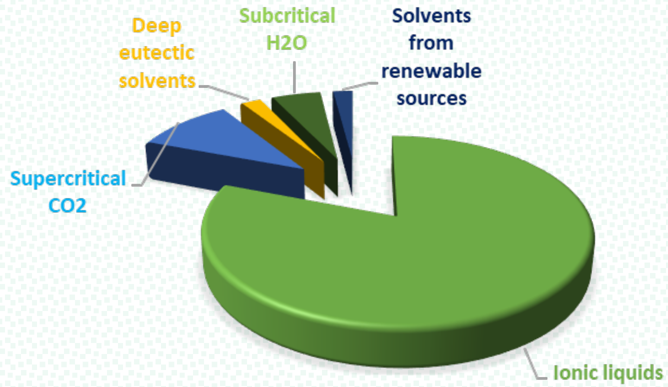


CYRENE®

dihydrolevoglucosenone



Dimethyl isosorbide (DMI)



* Bubalo et al., Green solvents for green technologies, J Chem Technol Biotechnol 2015; 90: 1631–1639

The membrane technology for microplastics removal

Membrane preparation

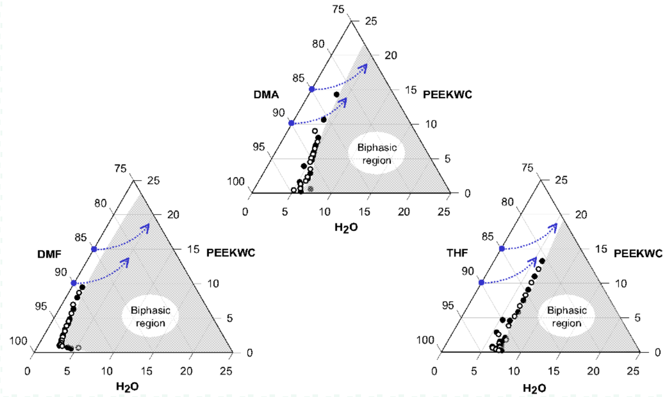
Phase inversion

Can be describe as a phase separation process: a one-phase solution containing the membrane polymer is transformed by a precipitation/solidification process into two separate phases (a polymer-rich solid and a polymer-lean liquid phase).

EIPS = *Evaporation induced phase separation*
VIPS = *Vapor induced phase separation*
TIPS = *Temperature induced phase separation*
NIPS/DIPS = *Non-Solvent induced or Diffusion induced phase separation*

FACTORS

- Choise of polymer, choise of solvent/non solvent
- Composition of casting solution
- Coposition of coagulation bath
- Temperature of casting solution and coagulation bath
- Evaporation time
- Presence of additives



* Figoli et al., Polymeric Membranes, Chapter 1, pp 1-44, In Membrane Fabrication, Edited by Nidal Hilal, Ahmad Fauzi Ismail, and Chris Wright, CRC Press, Print ISBN: 978-1-4822-1045-3; 2015

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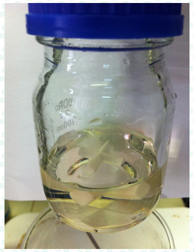
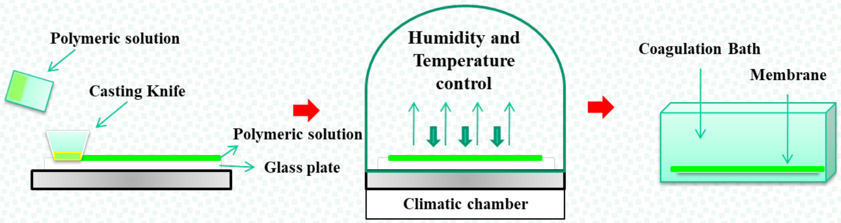
Membrane preparation

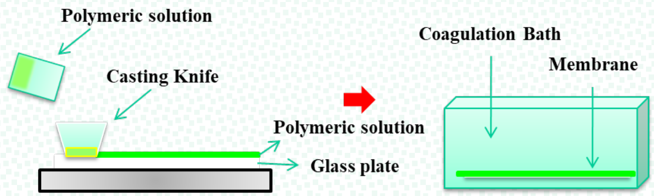


Phase inversion

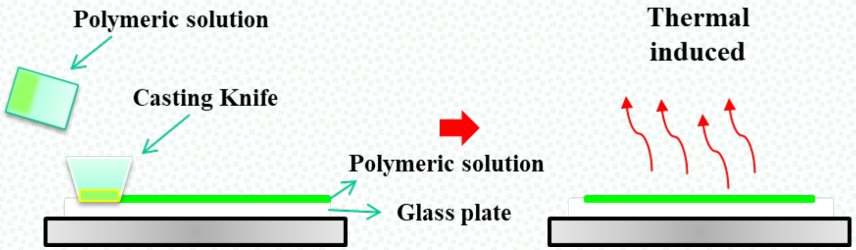
EIPS = Evaporation induced phase separation
VIPS = Vapor induced phase separation
TIPS = Temperature induced phase separation
NIPS/DIPS = Non-Solvent induced or Diffusion induced phase separation



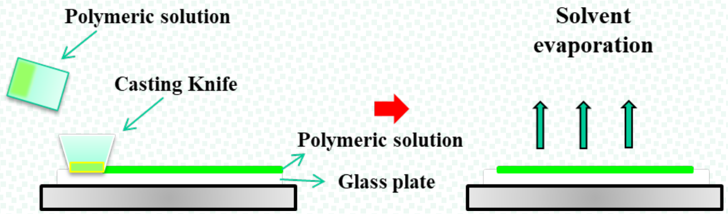
VIPS



NIPS



TIPS



EIPS

* Figoli et al., Polymeric Membranes, Chapter 1, pp 1-44, In Membrane Fabrication, Edited by Nidal Hilal, Ahmad Fauzi Ismail, and Chris Wright, CRC Press, Print ISBN: 978-1-4822-1045-3; 2015 .

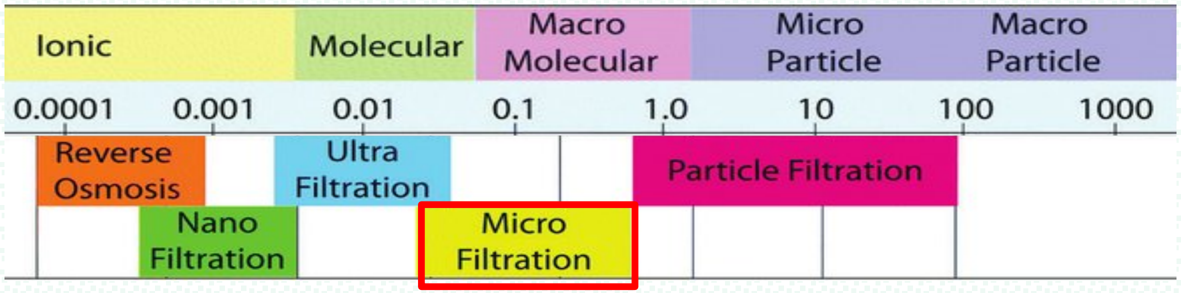
** F. Russo et a., Dimethyl Isosorbide As a Green Solvent for Sustainable Ultrafiltration and Microfiltration Membrane Preparation, ACS Sustainable Chem. Eng. 2019 .

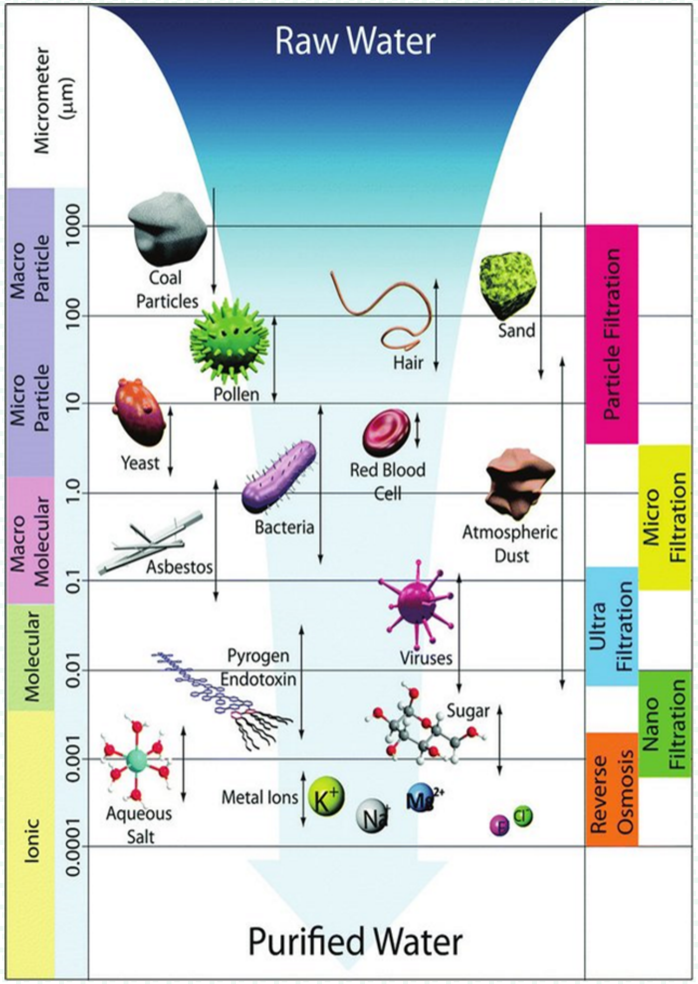
The membrane technology for microplastics removal

Membrane filtration

The application of membrane technology for micro-plastics removal has been also studied because membrane is suitable to remove low-density/poorly settling particles.

Membrane filtration spectrum





Membranes

- PORE SIZE : 0.2-0.4 µm
- PREPARATION TECHNIQUE: phase inversion
- Mostly direct interception capture at membrane surface.
- Secondary mechanisms of capture.

Filters

- PORE SIZE : > 0.2-0.4 µm
- Particles retained by “Direct Interception.”

* A. Lee et al., Membrane materials for water purification: design, development, and application, Environ. Sci.: Water Res. Technol., 2016, 2, 17

The membrane technology for microplastics removal

Membrane treatment for MP removal

Influencing factors and membrane process parameters to be considered for microplastic (MP)removal by membrane processes

	Influencing Factors	Membrane Process Parameters
Membrane process	Membrane material Membrane pore size Membrane thickness Membrane surface properties Source of polluted water (Seawater, surface water, municipal water, industrial wastewater etc.)	-Flux -Transmembrane pressure (TMP) -Polarization concentration -Cake layer formation and fouling -Rejection/Removal -Specific energy consumption (SEC)
Micro-Nanoplastic	Shape Size Mass Chemical composition Concentration	

*T. Poerio, E. Piacentini, R. Mazzei, Membrane processes for microplastic removal, Molecules, 24 (2019), 4148.

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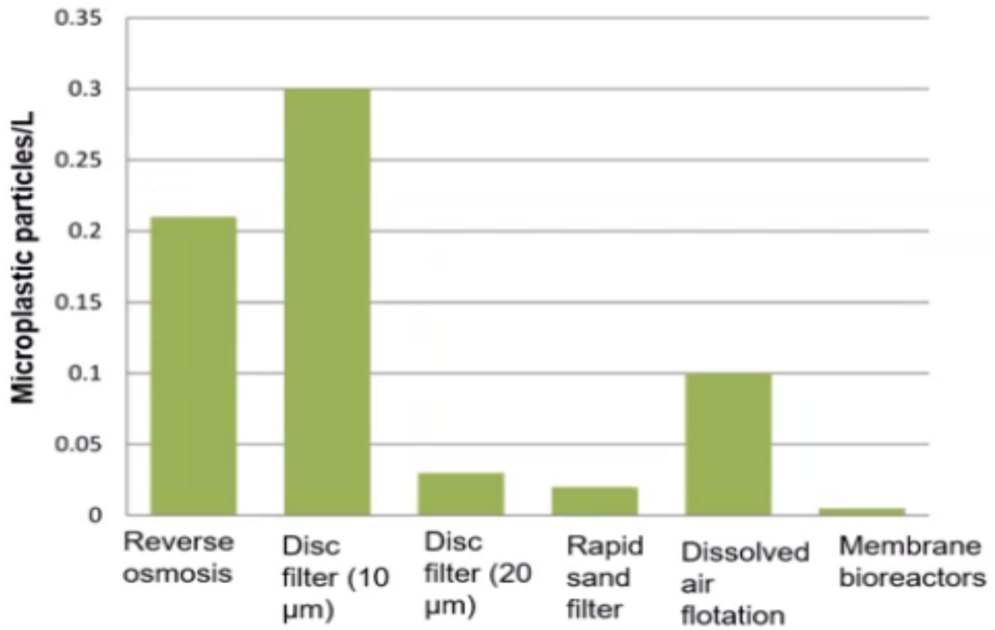
The membrane technology for microplastics removal

Membrane processes for MP removal

- ✓ Ultrafiltration (UF)
- ✓ Reverse Osmosis (RO)
- ✓ Membrane Bioreactor (MBR)

The shape of the plastic particles affects their removal efficiency in membrane watertreatment and can determine the interaction between other contaminants or microorganisms

The number of microplastic particles per liter in the final euent of each wastewater treatment plant



(Data elaborated from Ziajahromi et al. 2017 and Talvitie et al. 2017)

*T. Poerio, E. Piacentini, R. Mazzei, Membrane processes for microplastic removal, Molecules, 24 (2019), 4148.

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Membrane processes for MP removal

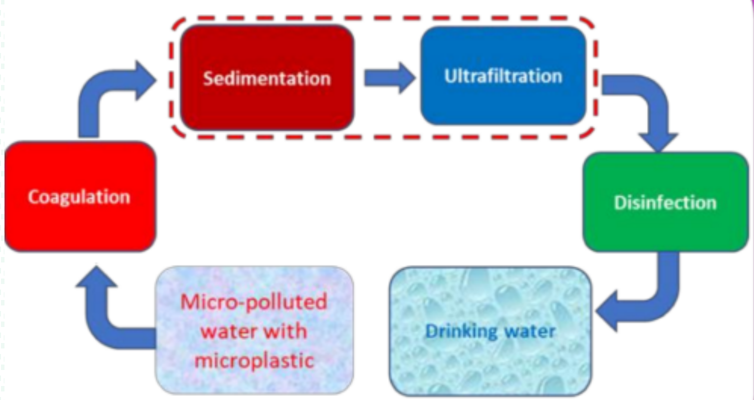
✓ Ultrafiltration (UF)

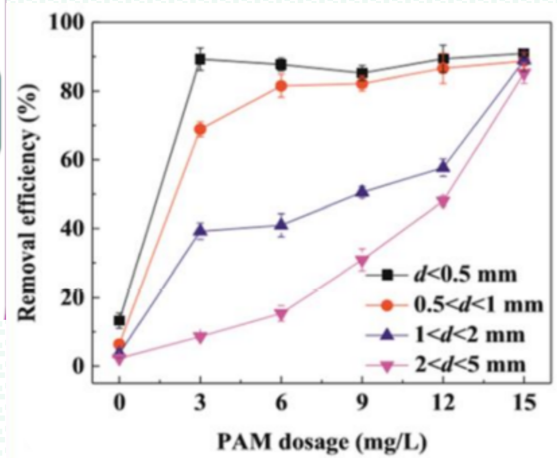
It is a low-pressure process (1–10 bar) that, using asymmetric UF membranes having a pore size between 1–100 nm.

UF, despite a broad molecular weight cut o (MWCO) range, is less active in removing low molecular weight organic matters. In many cases, UF is integrated into the process, using primary (flotation and filtration) and some secondary treatments as pretreatment stages and used for pre-filtration in reverse-osmosis plants to protect the reverse-osmosis process.

Study of microplastic removal by coagulation and UF process for the production of drinking water

The removal behavior of polyethylene (PE) in drinking water treatment by ultrafiltration and coagulation processes by using an Fe-based coagulant.





Low removal efficiency of PE particles (below 15%) was observed after coagulation, indicating the infectiveness of the sole coagulation process with respect to microplastic removal. However, when the Polyacrylamide (PAM) was added to enhance the coagulation performance, removal efficiency of small-particle-size PE (d < 0.5 mm) significantly increased from 13 to 91%.

*Ma, B.; Xue, W.; Hu, C.; Liu, H.; Qu, J.; Li, L. Characteristics of microplastic removal via coagulation and ultrafiltration during drinking water treatment. Chem. Eng. J. **2019**, 359, 159–167.

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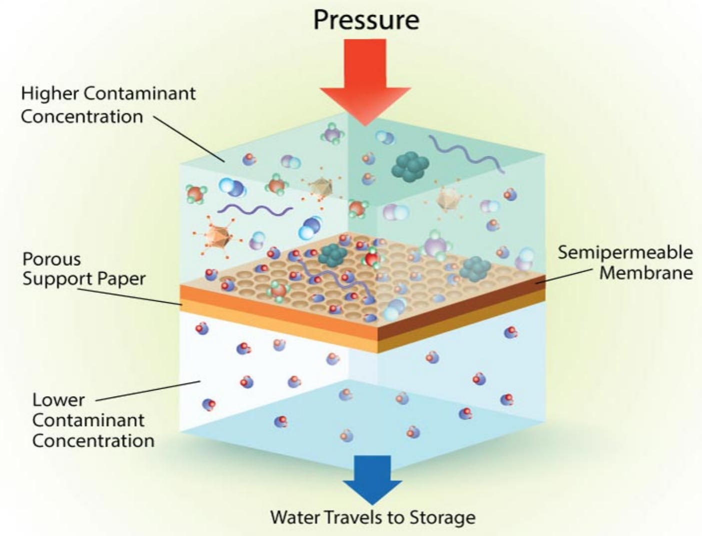
The membrane technology for microplastics removal

Membrane processes for MP removal

✓ Reverse Osmosis (RO)

Reverse Osmosis (RO), is actually used in municipal and industrial water treatment systems to purify water using nonporous or nanofiltration membranes (pore size > 2 nm) by removing salts, contaminants, heavy metals, and other impurities. It works by applying a high pressure (10–100 bar) to a concentrated water solution that forces the water through a semipermeable membrane, leaving all the other substances essentially in a more concentrated water solution.



Disadvantages

- Fuouling
- Scaling
- Need of pre-treatment steps

Most of the more performant applications of RO in the microplastic removal are obtained when coupled with membrane bioreactor technology.

*http://www.water-rightgroup.com/blog/how-do-reverse-osmosis-drinking-water-systems-work/

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The membrane technology for microplastics removal

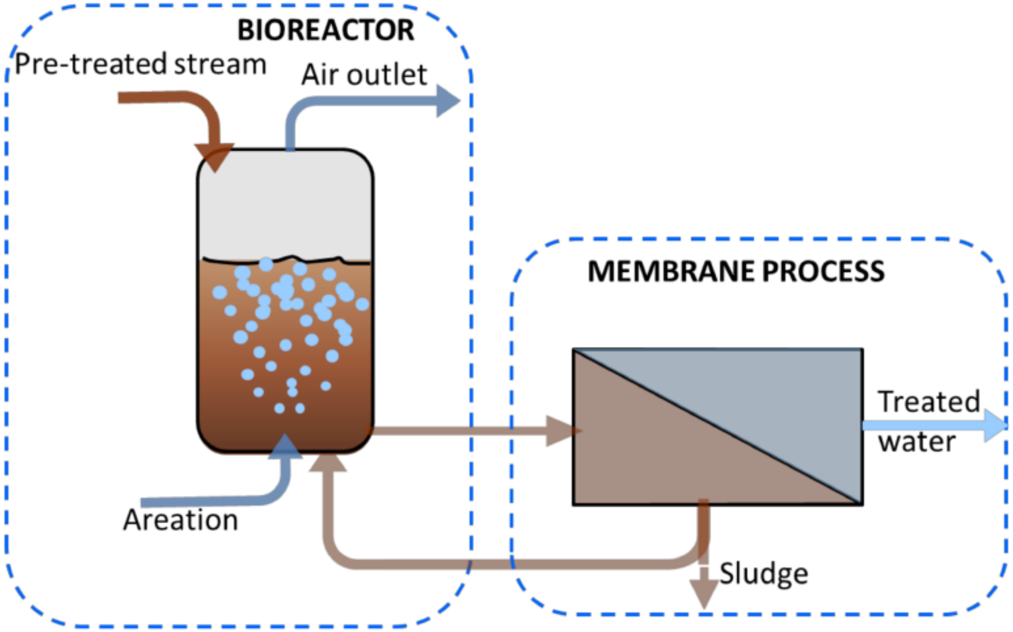
Membrane processes for MP removal

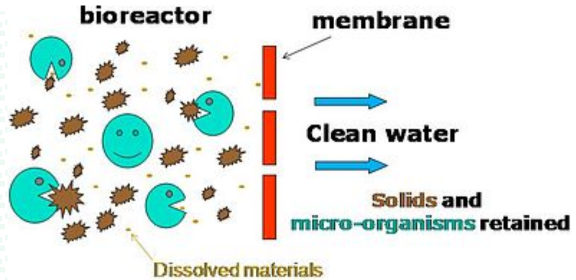
✓ Membrane Bioreactor (MBR)

Membrane bioreactor (MBR) are systems in which catalysis promoted by biological catalysts (bacteria, enzymes), is coupled to a separation process, operated by a membrane system (generally microfiltration or ultrafiltration).

In MP treatment, the role of MBR is the decrease of solution complexity by the biodegradation of the organic matter; this will permit the purification of MP and its further treatment. The process generally starts when a pre-treated streams enters in the bioreactor, where the process of biodegradation of organic matter is carried out. The produced mixed liquor is then pumped along with semi-crossflow filtration system for the separation process. Thanks to the membrane process, the MP is concentrated in the retentate stream.

Schematic representation of a MBR process





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The membrane technology for microplastics removal

The future for MP removal

New Solution for plastic removal…..on spot…and

Litter Hunter", system developed by a start-up Green Tech Solution (Naples)…..drone identify the plastic and the catamaran collect it (http://www.greentechsolution.it/)

WASTE SHARKER (www.wastsharker.com)

Combining with degradation devices

Thank you
for your attention!!

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