POLITECNICO DI TORINO
Collegio di Ingegneria Chimica e dei Materiali

Master of Science Course
in Materials Engineering

Master of Science Thesis

Microplastics removal from discharge water: mitigation actions, overview and research perspectives

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"You are the light of the world.
[…] Nor do people light a lamp
and put it under a basket,
but on a stand,
and it gives light to all in the house."
Mt 5: 14-16

Dedicata a chi nella mia vita è Luce:
è grazie a voi che il buio fa meno paura.
Con immensa gratitudine.

POLITECNICO DI TORINO
Collegio di Ingegneria Chimica e dei Materiali
Corso di Laurea Magistrale in Ingegneria dei Materiali

Riassunto della Tesi di Laurea Magistrale (Sessione: Dicembre 2020)

"Microplastics removal from discharge water: mitigation actions, overview and research perspectives"

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1. Scopo, Metodo e Obiettivi raggiunti

Questo lavoro di tesi si propone come prosecuzione ed estensione del lavoro svolto in occasione della Challenge proposta dal Politecnico di Torino in collaborazione con Rold, azienda italiana che si occupa della produzione di componentistica per elettrodomestici. Tale iniziativa, il cui titolo era *"CLEAR - miCro pLastic freE wAteR"*, aveva come obiettivo la costituzione di un team multidisciplinare per la progettazione di un dispositivo impiantabile nelle lavatrici di uso domestico per provare a mitigare l'emissione di microplastiche, nello specifico originate dagli abiti di origine sintetica durante i lavaggi.

Scopo di questo elaborato è provare a fornire una visione quanto più completa e accurata dei metodi di rimozione dalle acque di scarico attualmente disponibili. Si presentano sia le tecnologie sviluppate su scala di laboratorio che quelle proposte su scala industriale. Vengono, inoltre, presentati metodi di prevenzione che possono essere applicati ai materiali per prevenire la produzione di microplastiche di origine tessile.

Al fine di raggiungere tale obiettivo, si ricorre ad un'attenta ricerca bibliografica ed alla lettura di articoli selezionati e atti di convegno. In particolare, per ciascuno dei processi selezionati, sono state riportate le peculiarità e sono stati evidenziati i principali limiti, in maniera tale da fornire un quadro quanto più possibile oggettivo.

Si propone, inoltre, un breve progetto di ricerca che estenda il quadro di analisi dalle microplastiche alle nanoplastiche.

Il quadro emerso da tale ricerca evidenzia come, allo stato dell'arte, nessuna tecnica possa garantire tassi di rimozione del 100%. L'idea che ne deriva è quella di provare a creare dei sistemi che possano applicare simultaneamente due o più dei processi selezionati. Inoltre, considerando che in generale tutti i metodi di rimozione hanno evidenziato nelle limitazioni nella rimozione delle frazioni di microplastiche di più piccola dimensione, si dimostra necessario intervenire a monte sia sui materiali, applicando e creando dei trattamenti che limitino il deterioramento delle fibre e degli oggetti massivi a base polimerica, sia a livello legislativo con azioni concrete che limitino la produzione di prodotti contenenti microplastiche, come ad esempio prodotti per la cura personale.

2. Introduzione alla tematica

L'utilizzo di materiali plastici è in costante aumento. Questo perché si tratta di materiali in grado di garantire eccellenti *performance* con un costo di produzione assolutamente contenuto. Alcune delle proprietà che più si apprezzano in questi materiali sono, ad esempio, la bassa densità, le basse conducibilità elettriche e termiche, la resistenza a corrosione, le proprietà barriera garantite da molti di essi contro acqua e ossigeno.

Tuttavia, i materiali plastici subiscono facilmente degradazione, ovvero le macromolecole risultano progressivamente alterate a livello strutturale e chimico ed il materiale non può più, pertanto, garantire le condizioni di esercizio previste in fase di progetto.

Tra i vari fattori che possono determinare questi processi di degradazione si trovano raggi UV, calore, acqua, azioni meccaniche, fuoco. Molto spesso, queste alterazioni chimiche e strutturali portano, a loro volta, ad avere dei fenomeni di frammentazione dei materiali plastici. Tali frammenti risultano particolarmente pericolosi, in quanto possono facilmente essere ingeriti dagli organismi marini e conseguentemente entrano nella catena alimentare.

Di recente, questo fenomeno ha iniziato ad attirare le attenzioni della comunità scientifica. Tale fermento si è tradotto in un elevato numero di pubblicazioni scientifiche nell'ultimo triennio (2017-2020) e contestualmente anche in potenziali interventi legislativi volti a sancire un livello massimo di emissione e l'abolizione di prodotti di consumo, soprattutto del settore cosmetico, contenenti per formulazione microplastiche. A tal proposito, si segnalano due iniziative: nel 2019, l'ECHA, l'Agenzia Chimica Europea, ha proposto il banno delle Microplastiche dalla formulazione di prodotti per la cura del corpo e tale iniziativa dovrebbe divenire effettiva a partire dal 2030 e contestualmente l'OMS, Organizzazione Mondiale della Sanità, ha iniziato a studiare con grande attenzione le possibili conseguenze dell'ingestione di microplastiche sulla salute umana.

Lo studio di questo fenomeno è risultato storicamente ostacolato dalla mancanza di una definizione chiara e disambigua di microplastiche. Allo stato attuale, si riconosce internazionalmente come definizione quella proposta dal GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection) per cui, con la parola microplastiche, si vanno a definire i frammenti plastici di dimensione inferiore a 5 mm, incluse le particelle in range nanometrico. Tuttavia, le microplastiche possono essere caratterizzate da forme (fibrosa, aciculare, sferica, cluster, …) e colori diversi e proprio in funzione di queste caratteristiche possono cambiare i meccanismi di ingestione da parte degli organismi marini.

Mentre le prime osservazioni di *isole di plastica* nei giacimenti acquiferi (laghi, mari, oceani) risalgono ai primi anni Settanta, l'individuazione di microplastiche è solo più recente. In merito alla loro natura chimica, analisi spettroscopiche condotte sui campioni raccolti, evidenziano come queste siano perlopiù composte da materiali termoplastici ed in particolare da Polietilene (PE), Polipropilene (PP), Polivinilcloruro (PVC), Polistirene (PS) e Polietilentereftalato (PET). Inoltre, molto spesso sono state campionate fibre di Poliammide (PA). Meno frequente è la campionatura e l'individuazione di materiali termoindurenti. Tra questi, i più comuni sono schiume di poliuretano, adesivi e vernici perossidiche, compositi e gomme.

Invece, in relazione alla loro origine, queste vengono classificate in:

- Primarie, quando vengono emesse direttamente in acqua. È il caso delle microplastiche contenute nei cosmetici, delle fibre prodotte dal lavaggio di capi sintetici, dagli scarti dei processi di lavorazione e riciclo delle materie plastiche.
- Secondarie, quando derivano dalla degradazione di oggetti massivi in plastica.

I meccanismi di degradazione dei polimeri sono essenzialmente quattro: fotodegradazione, degradazione termo-ossidativa, degradazione idrolitica e biodegradazione da parte di microrganismi. I processi di degradazione riducono il peso molecolare medio del polimero, alterandone le proprietà strutturali, e modificano la sua struttura chimica, influenzandone le caratteristiche funzionali. La degradazione di polimeri come LDPE (polietilene a bassa densità), HDPE (polietilene ad alta densità), PP e PA esposti all'ambiente marino, è generalmente guidata dalla loro interazione con la componente ultravioletta (UV) della radiazione solare. La radiazione UV fornisce l'energia di attivazione necessaria per avviare l'ossidazione dei polimeri (degradazione foto-ossidativa), che diventano fragili e iniziano a frammentarsi in parti più piccole. Una volta avviato, il processo di degradazione può anche procedere termo-ossidativamente per qualche tempo senza ulteriore esposizione alla radiazione UV. Dopo diversi passaggi di frammentazione, le catene polimeriche raggiungono un peso molecolare e una dimensione nettamente minori e in tal modo le materie plastiche riescono ad essere metabolizzate da microrganismi, che convertono il carbonio presente nelle catene polimeriche in anidride carbonica o lo incorporano in biomolecole. Questo processo viene chiamato *biodegradazione*. Tuttavia, in ambiente marino, quest'ultimo processo è di diversi ordini di grandezza più lento rispetto alla degradazione ossidativa indotta dalla radiazione UV. Questo ritardo è principalmente il risultato delle temperature relativamente più basse e della minore concentrazione di ossigeno nell'acqua di mare. Un altro fattore che influenza la velocità della biodegradazione è il cosiddetto *fouling*, ovvero la formazione di un biofilm sulla superficie degli oggetti in plastica. L'idrolisi, invece, di solito non è un meccanismo di degradazione significativo in acqua marina.

Anche l'azione meccanica può originare fenomeni di degradazione sui materiali plastici. Questo è quanto accade, ad esempio, nelle lavatrici domestiche ed industriali dove, a causa dei fenomeni di attrito, si liberano dalle fibre tessili numerose microplastiche. Come riportato da Julien Boucher e Damien Friot nel loro rapporto per la IUCN (International Union for Conservation of Nature) [1], il consumo annuale globale di fibre per il settore moda è aumentato negli ultimi due decenni (+ 79,3% tra il 1992 e il 2010). Questa crescita è quasi esclusivamente dovuta all'aumento del consumo di fibre sintetiche con un incremento vicino al 300% (da 16 a 42 milioni di tonnellate) rispetto allo stesso periodo. Di conseguenza, il 35% delle microplastiche primarie scaricate in acqua proviene da tessuti sintetici che originano piccoli frammenti all'interno della lavatrice. I dati sulle principali sorgenti di Microplastiche sono riportati in Figura I.

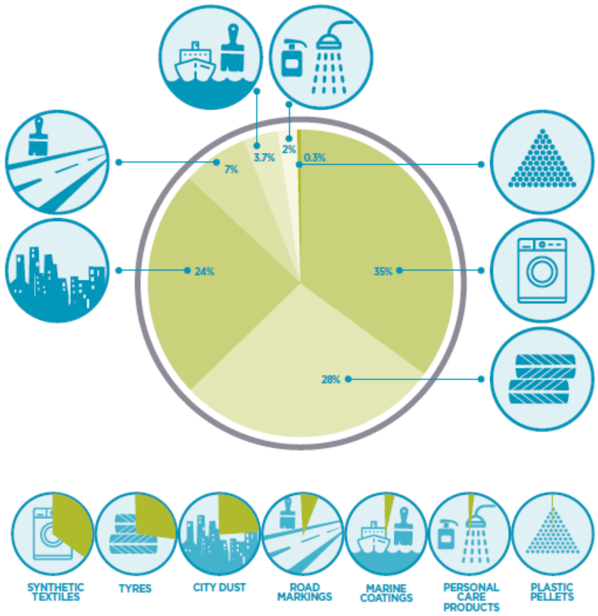

Figura I- Fonti delle microplastiche globalmente rilasciate negli oceani [1]

Recentissimi studi [2, 3], risalenti a luglio 2020, dimostrano come le mascherine chirurgiche, utilizzate come dispositivi di protezione individuale in fase di pandemia da CoVid-19, siano sorgenti di microplastiche. Queste sono infatti composte di polipropilene, poliestere e poliammide sotto forma di fibre facilmente degradabili con l'utilizzo e il conseguente attrito meccanico che ne deriva, fino a formare dei frammenti fibrosi di lunghezza critica inferiore ai 5 mm.

3. Quadro generale degli interventi

La Figura II riporta il quadro generale degli interventi mirati alla riduzione dell'emissione di microplastiche in acqua. È possibile ricorrere a un duplice approccio: intervenire a monte, con azioni di mitigazione che evitino che queste vengano prodotte e intervenire simultaneamente a valle, con azioni di rimozione che vadano a evitare che queste siano emesse in acqua. Le azioni di rimozione possono essere basate su diversi principi di funzionamento: chimico, fisico e biologico e molte sperimentazioni sono state finora condotte solo a livello di laboratorio. Tuttavia, le tecniche basate su un principio di funzionamento fisico, sono in parte già utilizzate per altri inquinanti, sotto forma di particolato solido, negli impianti di trattamento acque.

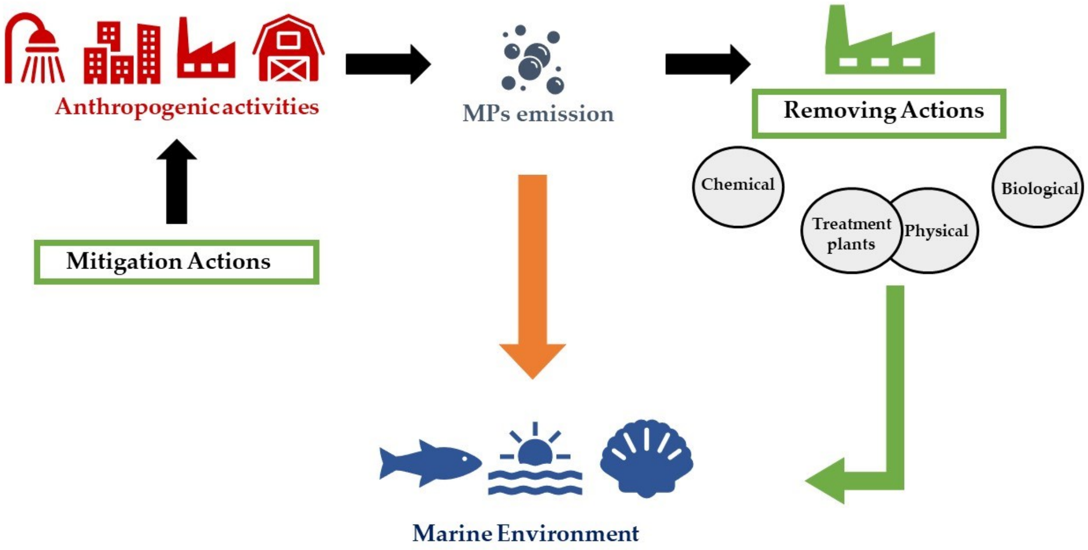

Figura II- Quadro generale degli interventi proposti nell'elaborato

Le varie tipologie di intervento verranno adesso introdotte singolarmente.

4. Azioni preventive e mitigative

Lo scopo di questa prima indagine è descrivere le idee più recenti per prevenire l'emissione di microplastiche primarie in acqua. Questo tipo di inquinante proviene principalmente da fonti antropiche, sia industriali che domestiche e quindi da beni di consumo. Purtroppo, considerando che solo di recente si è sviluppata una sensibilità verso questa tematica, le ricerche scientifiche sulle azioni preventive sono riservate a pochi settori di interesse. Tra questi, il settore della produzione di fibre tessili per l'abbigliamento. De Falco *et al.* [4, 5] hanno proposto in merito lo sviluppo di trattamenti di superficie, compatibili con i processi già esistenti dell'industria tessile, che vadano a *sigillare* le fibre e contestualmente ad agire da lubrificante per limitare l'azione dell'attrito meccanico. Le sostanze scelte per sviluppare questi trattamenti sono, rispettivamente, la pectina, un polisaccaride naturale presente nelle pareti delle piante, l'acido polilattico (PLA) ed infine un copolimero di polibutilene succinato e butilene adipato (PBSA) e sono stati testati sulla superficie di una poliammide. Tutti queste sostanze sono ecocompatibili e sostenibili ed i risultati raggiunti evidenziano una riduzione del tasso di produzione di microplastiche rispettivamente del 90%, 80% e 80%. Questi risultati sono sicuramente molto promettenti: oltre a garantire una mitigazione del fenomeno, si può evidenziare come questi trattamenti non vadano a compromettere l'aspetto estetico della fibra (come si può osservare in Figura III), aspetto cruciale per il settore moda. Uno dei punti più critici, su cui sarà ancora necessario intervenire, è la scarsa durata di questi rivestimenti.

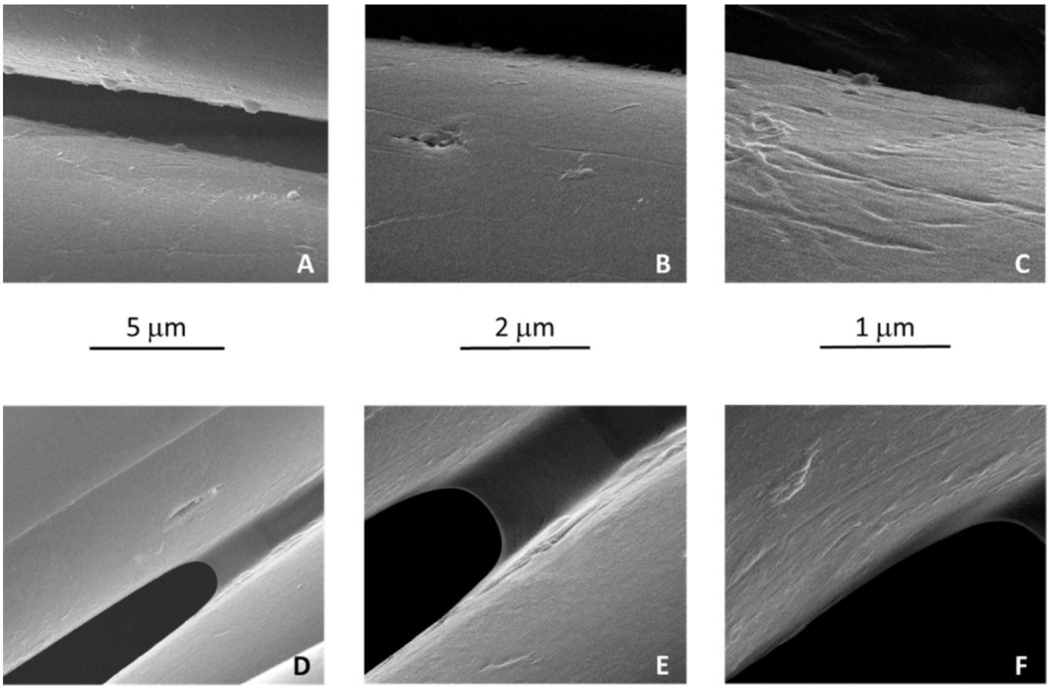

Figura III-Micrografie SEM. Superfici A – C) PA senza trattamento e superfici D – F) PA rivestita da trattamento a base pectina [4]

5. Metodi ispirati alla rimozione di particolato solido

I primi studi condotti sulla rimozione di microplastiche si basavano essenzialmente sugli stessi principi di funzionamento utilizzati per la depurazione dell'acqua applicati al particolato solido negli impianti di trattamento delle acque reflue (WWTP) o negli impianti di trattamento per l'acqua potabile (WTP). Un tipico WWTP viene riportato in Figura IV. Questi studi hanno essenzialmente testato gli impianti già esistenti e la loro efficienza nella rimozione di microplastiche, campionando l'acqua in ingresso e quella trattata. Una delle questioni più controverse connesse a questo argomento è la necessità di una procedura standard per l'isolamento, l'elaborazione e l'identificazione delle microplastiche nei campioni di acque reflue, al fine di ottenere risultati confrontabili e coerenti. Allo stato dell'arte, mancano procedure standard per la raccolta e l'analisi di campioni di microplastiche. Il campionamento non è semplice, a causa delle dimensioni delle particelle e della composizione dei materiali plastici. Le materie plastiche, infatti, sono ottenute dalla combinazione di polimero vergine con cariche e additivi che possono creare difficoltà nell'identificazione del tipo di polimero. Altri problemi che possono emergere sono la carica elettrostatica sulla superficie delle particelle, la formazione di schiuma o una bassa separabilità dai fanghi di scarico.

Nonostante la mancanza di una procedura comune, di recente sono stati condotti vari studi ed i risultati ottenuti mostrano diversi punti in comune. Oltre ad un'analisi quantitativa, diversi autori hanno proposto anche un'analisi qualitativa con l'obiettivo di identificare i principali polimeri presenti nelle microplastiche. Queste analisi sono tipicamente condotte attraverso tecniche spettroscopiche non distruttive, come la spettroscopia a infrarossi a trasformata di Fourier (FTIR) o la spettroscopia μ-FTIR e Raman o μ-Raman.

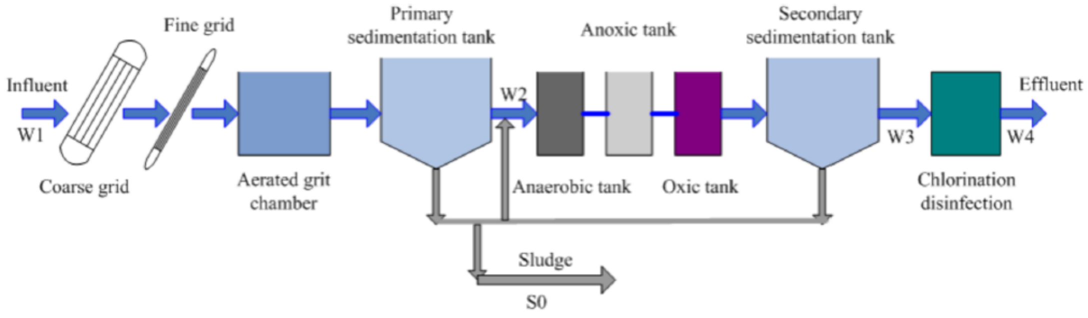

Figura IV-Step di trattamento in un tipico impianto di trattamento acque reflue [6]

I processi di trattamento tradizionali, sia per le acque reflue che per l'acqua potabile, si sono rivelati promettenti per la rimozione di microplastiche ed hanno a loro volta ispirato diverse ricerche a livello di laboratorio. Queste ricerche hanno tutte dimostrato che l'aggiunta di una fase finale avanzata di trattamento (*fase terziaria*) può migliorare il tasso di rimozione dell'impianto. Riepilogando i risultati emersi dallo studio di questi trattamenti, si osservano diversi punti in comune:

- Microplastiche di più piccola dimensione (1-10μm o fino a 100 μm se non è prevista una fase di trattamento avanzato terziario) non vengono facilmente ritenute dagli impianti già esistenti;
- L'analisi chimica ha rivelato che i polimeri più comuni presenti sono PET, PP, PE e PA, spesso con una morfologia fibrosa;
- Una fase di trattamento terziaria (coagulazione, filtro a sabbia, RFS[1], GAC[2], DC[3], CASP[4], MBR[5], ozonizzazione) è necessaria per ottenere elevati tassi di rimozione di microplastiche.

Molti punti restano però aperti. In particolare, è necessario andare a definire la distribuzione granulometrica delle microplastiche nelle acque da trattare, ottenibile solo attraverso un'accurata analisi statistica, e l'interazione tra le microplastiche e altri inquinanti tipicamente presenti in acqua.

Nei paragrafi successivi vengono introdotte le principali tecniche sperimentali sviluppate a livello di laboratorio, suddivise in funzione del loro principio di funzionamento: chimico, fisico o degradazione biologica.

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[1] RSF: Rapid Sand Filter
[2] GAC: Granular Activated Carbon
[3] DC: Disc Filter
[4] CASP: Conventional Activated Slug Process
[5] MBR: Membrane Bioreactor

6. Metodi basati su principi chimici di funzionamento

Gli impianti di trattamento acque hanno evidenziato diversi limiti nella rimozione di microplastiche. Di conseguenza, sono state sviluppate numerose tecniche innovative, principalmente su scala di laboratorio. Questo paragrafo introduce i principali metodi chimici testati allo stato dell'arte.

Queste tecniche possono essere grossolanamente suddivise in due macrocategorie, descritte nei paragrafi successivi.

6.1 Metodi per agglomerazione

La maggior parte di queste tecniche si basa essenzialmente su reazioni chimiche o elettrochimiche che inducono l'agglomerazione di MP nel sistema acquoso. I polimeri che costituiscono le microplastiche hanno densità prossime a quelle dell'acqua (1 g/cm^3), come evidente in Tabella I e, per questo motivo, si trovano generalmente sospese in acqua.

Tabella I-Densità dei principali polimeri costituenti le microplastiche. Adattato da [7]

Material	**Density [g/cm^3]**
Polyethylene (PE)	0.91-0.96
Polypropylene (PP)	0.90-0.91
Poly-vinylchloride (PVC)	1.16-1.55
Polystyrene (PS)	1.05
Poly-ethyleneterephthalate (PET)	1.37
Polyamide 66 (PA66)	1.14
Polyurethane (PU)	1.05-1.21

Conseguentemente, si intende promuovere processi che portino alla formazione di aggregati che, avendo una maggiore massa, riescano a sedimentare velocemente. In questo modo, la separazione delle microplastiche dal sistema acquoso risulterà favorita. Tale aggregazione può essere indotta mediante una reazione sol-gel o mediante sali. Nel primo caso, si aggiungono al sistema i precursori per una reazione sol-gel, ad esempio alcossisilani [8]. Le reazioni sol-gel avvengono mediante due step: idrolisi e condensazione e portano ad ottenere un *network* in grado di attrarre, tramite interazioni di Van Der Waals, le microplastiche che, pertanto, restano intrappolate in aggregati di massa maggiore, più semplici da separare anche solo per filtrazione. Lo stesso risultato si può ottenere anche utilizzando sali di alluminio o ferro [9, 10] che, in specifiche condizioni di pH, tendono a formare flocculi in grado di intrappolare le particelle plastiche o ancora mediante un processo elettrochimico. In quest'ultimo caso, sotto l'azione di un campo elettrico esterno, gli ioni metallici (generalmente Fe^{3+} o Al^{3+}) vengono generati da elettrodi sacrificali ed entrano nel flusso d'acqua. Simultaneamente, questi cationi possono ricombinarsi con gruppi idrossili in acqua, formando idrossidi metallici che agiscono come micro-coagulanti all'interno del sistema, destabilizzando la carica superficiale dei solidi sospesi. Quest'ultimo processo è riepilogato in Figura V.

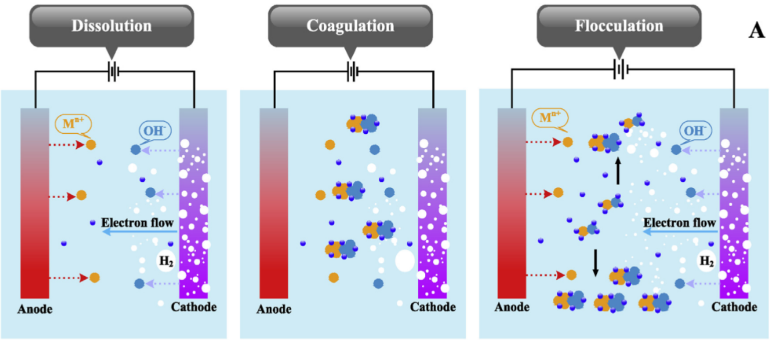


Figura V- Elettrocoagulazione indotta in un sistema acquoso contenente microplastiche [11]

Uno dei principali svantaggi di questi processi è il potenziale impatto ambientale dei reagenti utilizzati.

6.2 Fotocatalisi

La fotocatalisi è stata solo di recente testata in questo ambito. In particolare, si sfrutta la degradazione dei polimeri che costituiscono le microplastiche indotta dalla fotocatalisi: in questo modo, si ottengono sostanze chimiche meno inquinanti. Brevemente, la degradazione fotocatalitica si verifica quando un semiconduttore è esposto a una sorgente di fotoni che emettono luce con energia uguale o superiore al suo band gap, generando lacune (h^+) ed elettroni eccitati (e^-). Le lacune, combinate con acqua (H_2O) o gruppi idrossilici (OH^-), generano radicali idrossilici (OH•) che sono specie altamente ossidanti in grado di degradare molti inquinanti organici, generando diverse sostanze chimiche. Ariza-Tarazona et *al.* [12] hanno testato l'efficacia dell'N-TiO_2 come semiconduttore per degradare l'HDPE estratto da uno scrub disponibile in commercio. Al fine di sviluppare un processo che fosse più sostenibile nella sua interezza, il semiconduttore è stato ottenuto mediante un processo di sintesi *bio-ispirato* a partire da scarti alimentari, nello specifico gusci di cozze. Lo stesso test è stato ripetuto con un N-TiO_2 ottenuto mediante una tradizionale sintesi sol-gel. Gli esperimenti fotocatalitici eseguiti con le polveri di N-TiO_2 derivate dalle cozze sono stati effettuati utilizzando film compositi di N-TiO_2/microplastiche. La degradazione della plastica è stata valutata dalla perdita di peso e dallo studio dei cambiamenti chimici e morfologici, confermati da FTIR e SEM. Un secondo test fotocatalitico è stato condotto utilizzando un composito HDPE/N-TiO_2 in mezzo acquoso a temperatura ambiente. Si è concluso che l'N-TiO_2 derivato dai gusci delle cozze, presenta un'eccellente capacità di promuovere la perdita di massa delle microplastiche, anche in ambiente acquoso. L'altro fotocatalizzatore, ottenuto tramite un processo sol-gel convenzionale e meno sostenibile, presenta anch'esso una buona capacità di promuovere la perdita di massa delle microplastiche. I risultati hanno inoltre evidenziato che le condizioni ambientali dovrebbero essere impostate o progettate con cura per evitare l'arresto della fotocatalisi. Tuttavia, questo processo è stato testato solo su scala di laboratorio e quindi dovrebbe essere adattato agli impianti di trattamento delle acque reflue

7. Metodi fisici per la rimozione di microplastiche

La categoria dei metodi fisici di rimozione è piuttosto ampia e include tecniche molto diverse tra loro. Questi, infatti, possono essere a loro volta suddivisi in base al loro peculiare principio di funzionamento. Il metodo di rimozione può essere, infatti, un'estrazione magnetica, un processo di adsorbimento o può essere basato su una tecnologia di filtrazione o ultrafiltrazione.

Queste tecniche, così come i metodi chimici introdotti nel paragrafo precedente, sono stati principalmente testati su scala di laboratorio. Le tecnologie di filtrazione e ultrafiltrazione sono, in parte, già state testate negli impianti di trattamento delle acque industriali (WWTP e WTP). Una delle tecniche più innovative prevede di ricorrere a un

fenomeno di estrazione magnetica di seguito descritto. Le particelle di plastica sono caratterizzate da una superficie idrofobica. Approfittando di questa peculiarità, Grbic *et al.* [13] hanno utilizzato nanoparticelle di Fe idrofobiche per funzionalizzare la superficie delle microplastiche, consentendone, pertanto, un recupero magnetico. La procedura è semplicemente schematizzata in Figura VI.

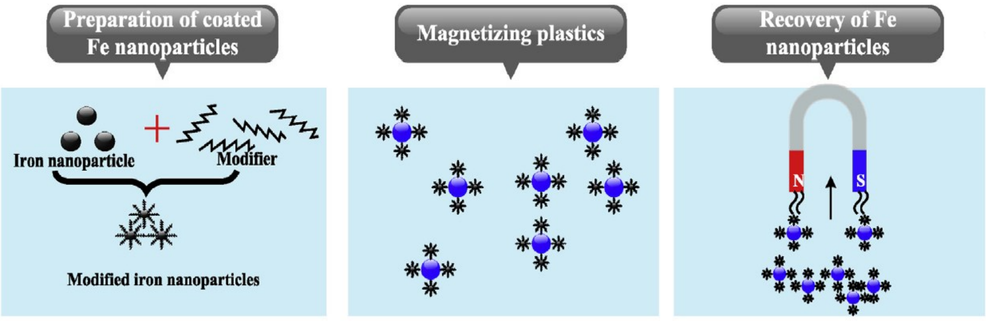


Figura VI- Processo di estrazione magnetica [11]

I risultati di questo studio hanno evidenziato un tasso di recupero del 92% per sfere di 10-20 μm di polietilene di polistirene e del 93% per microplastiche di dimensione superione a 1 mm (PE, PET, PS, poliuretano, PVC e PP) in acqua di mare. Inoltre, sono stati rimossi anche l'84% e il 78% di microplastiche (PE, PET, PS, poliuretano, PVC e PP) di dimensione compresa tra 200 μm e 1 mm rispettivamente in acqua dolce e da sedimenti marini. Ciò ha dimostrato che, nel complesso, la procedura è efficiente per varie dimensioni, tipi di polimeri e forme di campioni.

In alternativa, è possibile ricorrere a tecnologie a membrana, che hanno il vantaggio di garantire una qualità stabile per l’effluente. Inoltre, sono processi ormai ben noti. A seconda delle dimensioni della membrana e della pressione applicata, la tecnologia di separazione può essere classificata in ultrafiltrazione (1–100 nm, 1–10 bar), nanofiltrazione (1-2 nm, pressione fino a 50 bar) e osmosi inversa (0,1-1 nm, 10–100 bar). Il principio generale delle tecnologie di separazione a membrana per la purificazione delle acque è mostrato in Figura VII. Semplificando, si ha che, sotto l'applicazione di una differenza di pressione, la dimensione del poro della membrana viene utilizzata per intercettare le particelle presenti nelle acque reflue.

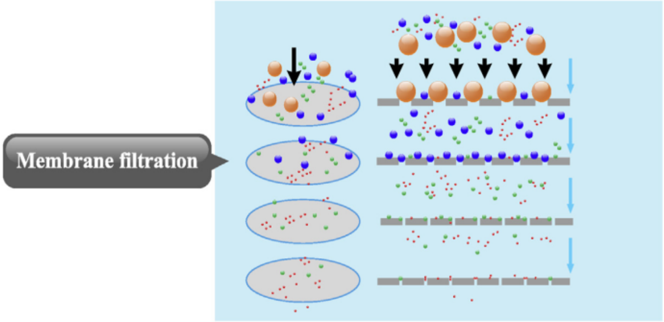


Figura VII-Filtrazione a membrana, schema generico di funzionamento

L'applicazione di tali tecnologie per la rimozione di microplastiche è ancora piuttosto limitata. Accanto a questi processi, si evidenziano i processi MBR (*Membrane Bio-Reactor*). Gli MBR sono sistemi in cui una catalisi promossa da catalizzatori biologici, come batteri ed enzimi, è accoppiata a un processo di separazione, gestito da un sistema a membrana nel range della microfiltrazione (100-1000 nm, pressioni fino a 5 bar) o dell'ultrafiltrazione. Il processo MBR è mostrato in Figura VIII. La membrana crea diversi compartimenti e di conseguenza può essere sviluppato un sistema di reazione eterogeneo controllato(organico/acqua) /multifase(liquido/gas). Le diverse fasi possono essere mantenute separate (come ad esempio in un processo di estrazione con solvente a membrana), oppure possono essere disperse l'una nell'altra (come in un processo di emulsificazione a membrana). Nello specifico, per quanto riguarda la rimozione di microplastiche, il processo inizia generalmente quando un flusso pretrattato entra nel bioreattore, favorendo un processo di biodegradazione della materia organica. Il liquido miscelato prodotto viene quindi pompato nella zona di separazione a membrana. Bayo et *al.* [14] hanno ottenuto un'efficienza di rimozione del 79,01% per le microplastiche, dimostrando la necessità di questo tipo di processo nei WTTP dopo le fasi primarie e secondarie.

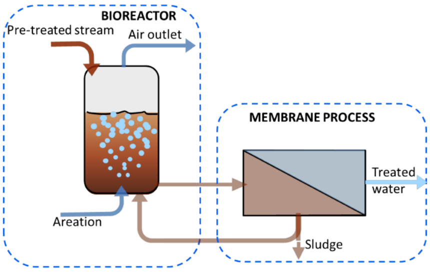


Figura VIII- Processo MBR [15]

Accanto a questi studi, altre ricerche recenti si sono piuttosto soffermate sulla possibilità di ottenere dei nanomateriali strutturati in maniera tale da riuscire ad "intrappolare" fisicamente le microplastiche. Queste ricerche partono da una conoscenza dei meccanismi di adsorbimento di microplastiche da parte di alcune specie marine (*fucus vesiculosus, tridacna maxima*) [16, 17]. In quest'ottica sono state valutate anche le performance di biochar [18] e di una spugna composita grafenossido e chitina [19].

8. Metodi biologici per la degradazione di microplastiche

Questa categoria di metodi è molto diversa dalle precedenti. Queste tecniche, infatti, si basano su un processo degradativo: le MP si trasformano in altre sostanze organiche meno inquinanti e non vengono rimosse fisicamente.

Si può, ad esempio, ricorrere ad un trattamento di biofiltrazione dell'acqua. In questo caso, l'acqua da trattare viene filtrata attraverso materiale organico poroso (detto anche letto filtrante) che funge da supporto, e in parte da nutrimento, per i microrganismi aerobici. Gli inquinanti trasportati dal flusso vengono metabolizzati dai microrganismi che in questo modo li trasformano in vari prodotti di reazione, acqua e anidride carbonica come sostanze di scarto.

Inoltre, in letteratura sono stati approfonditi i meccanismi di biodegradazione degli organismi marini per capire come questi possano avere un'influenza positiva sui tassi di rimozione delle microplastiche.

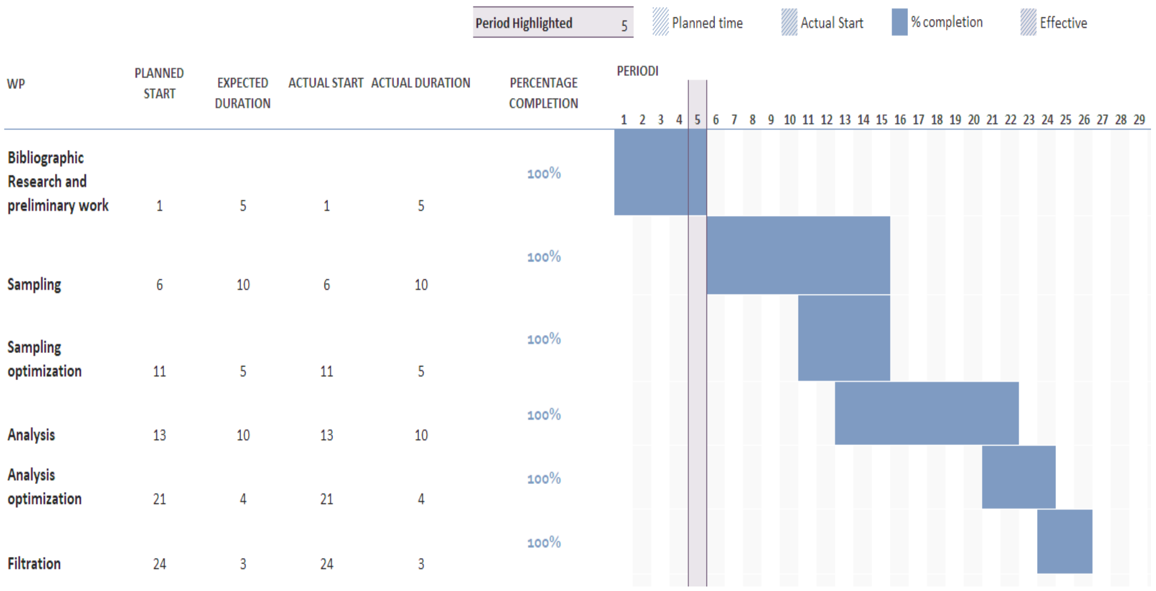
9. Progetto di ricerca

Ottimizzazione dei processi di campionatura e analisi per le nanoplastiche

La letteratura presentata e riassunta in questo lavoro di tesi riguarda i metodi di rimozione delle MP. Uno dei limiti emersi è che nessuno di questi metodi è efficace nella rimozione della frazione di più piccola dimensione delle MP; pertanto, questi sicuramente non sono efficaci nella rimozione delle particelle di plastica su scala nanometrica (1-100 nm), comunemente originate dal degrado delle materie plastiche. Molto recentemente, le nanoplastiche (NP) sono diventate oggetto di interesse per la comunità scientifica in quanto possono essere probabilmente considerate più dannose per la salute umana.

Come nel caso delle microplastiche, gli studi sulla loro tossicità sono ancora in una fase preliminare di studio e ciò è dovuto principalmente alle difficoltà nel trovare metodi analitici adeguati alla rilevazione di MP e soprattutto NP in matrici complesse. Molti dei lavori pubblicati hanno evidenziato che, per l'uomo, la principale fonte di assunzione di MP e NP è attraverso l'ingestione orale. Segue una serie di passaggi che coinvolgono le particelle ingerite con vari tipi di interazioni con l'organismo umano. Le particelle possono entrare in contatto con fluidi digestivi, cellule intestinali e organi come il fegato, oltre che essere espulse. Tutti questi fenomeni sono strettamente influenzati dalla dimensione delle particelle ingerite e dalla loro composizione. In particolare, l'attraversamento della barriera intestinale avviene in modo dipendente dalle dimensioni e solo particelle di plastica di dimensioni inferiori a 150 µm potrebbero, in linea di principio, attraversare l'epitelio intestinale. Questo è il motivo per cui l'ingestione di NP sembra essere più dannosa rispetto all'ingestione di particelle di plastica più grandi. Questo dato è allarmante, considerando che la maggior parte dei Food Contact Materials (FCM), per imballaggi o stoviglie, è costituita da plastica. Inoltre, le NP sono tipicamente idrofobiche e questa caratteristica, combinata con le dimensioni, consente il loro ingresso nelle cellule attraverso porazione o rottura delle pareti cellulari, che può portare a citotossicità. Questo effetto citotossico è già stato verificato per un'ampia gamma di nanomateriali, inclusi nanotubi di carbonio e nanoparticelle d'argento, e sono state sollevate preoccupazioni circa la mancanza di regolamenti sull'uso di nanoparticelle nei cosmetici e negli alimenti in Nord America ed Europa. Nonostante la potenziale gravità dei suoi impatti sull'ambiente e sulla salute, l'inquinamento da nanoplastiche è stato generalmente trascurato, principalmente a causa di sfide metodologiche.

In particolare, allo stato attuale, manca un metodo standard per la campionatura e l'analisi di nanoplastiche. Si propone, pertanto, un progetto strutturato in vari *work packages* (a loro volta suddivisi in *task* e *subtask*) da sviluppare in un arco di tempo stimato intorno ai 5 mesi. Le principali attività previste vengono riepilogate nel seguente diagramma di Gantt (Figura IX).



WP	PLANNED START	EXPECTED DURATION	ACTUAL START	ACTUAL DURATION	PERCENTAGE COMPLETION
Bibliographic Research and preliminary work	1	5	1	5	100%
Sampling	6	10	6	10	100%
Sampling optimization	11	5	11	5	100%
Analysis	13	10	13	10	100%
Analysis optimization	21	4	21	4	100%
Filtration	24	3	24	3	100%

Figura IX-Gantt Chart proposto per il progetto di ricerca

Tale progetto si pone un duplice obiettivo:

- Obiettivo 1: sviluppo di una procedura standard per il campionamento e l'analisi delle nanoplastiche (NP);
- Obiettivo 2: convalida della procedura sviluppata per filtrare NP utilizzando membrane nanoporose di grafene.

10. Conclusioni

Si presentano, per punti, i principali risultati ottenuti:

- Mediamente, per le tecniche analizzate, i tassi di rimozione sono superiori all'80% e le efficienze maggiori (superiori al 90%) si raggiungono solo se più tecniche vengono accoppiate tra loro. In particolare, negli impianti di trattamento acque deve essere previsto almeno uno stadio *terziario* di trattamento.
- In generale, i metodi sono poco efficaci nella rimozione della frazione più piccola ($1 - 10\mu m$ o fino a 100 μm se non è previsto uno stadio terziario di trattamento) di microplastiche e di certo si rivelano poco effettivi nella rimozione di nanoplastiche. Tali efficienze dovrebbero migliore ricorrendo a trattamenti preventivi sui materiali; tuttavia, allo stato attuale, mancano studi in tal senso.
- Le analisi chimiche effettuate hanno rivelato che i polimeri più comunemente presenti nelle microplastiche sono PET, PP, PE e PA, spesso con una morfologia fibrosa.
- Le nanoplastiche, secondo i primi studi emersi, sono più pericolose, in quanto in grado di penetrare nell'epitelio intestinale. Gli studi riguardanti le nanoplastiche sono stati a lungo rallentati dalla mancanza di una procedura standard per campionatura e analisi.

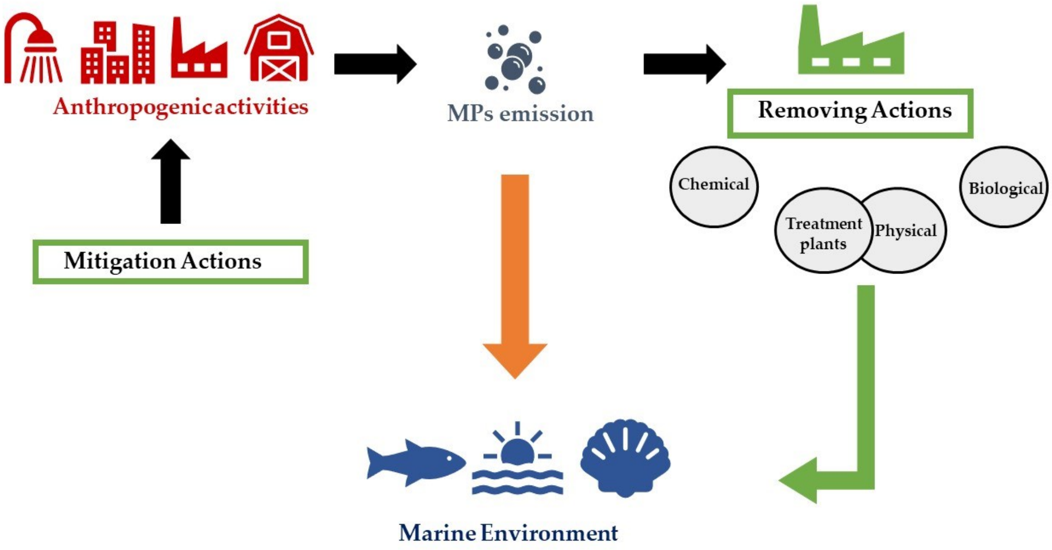
Abstract

The increasing use of plastic materials in different industrial fields is essentially due to their unique characteristics that make them optimal for a wide range of applications. This spreading has brought to the dispersion of plastic materials, fragments and objects in the environment.

This led to the rise of an insidious kind of pollution, strictly connected to the mechanical degradation of these materials which consists of the presence in the environment of "*plastic particles < 5 mm in diameter, which include particles in the nano-size range*", commonly known as microplastics (MPs). During the last decade, several studies have been conducted on MPs removal from discharge or drinking water. This topic is currently trending and even companies are showing a marked interest in this issue.

The first studies conducted on possible MPs removal methods have essentially replicated the same working principles of water purification applied to solid particulates in drinking water treatment plants or in wastewater plants. At present, several new removal methods are under investigation and these can be classified in chemical, physical and biological depending on their basic working principle. This work also presents mitigative actions, consisting of surface treatments that can be implemented on clothes fibers to avoid MPs release in water. The advantages and drawbacks of various removal mechanisms are discussed.

Besides, research perspectives are presented. In particular, the last part of this thesis proposes a possible research path for the development of a standard procedure for sampling and analyzing nanoplastics, i.e. the fraction of MPs in the nano size range.



Graphical Abstract

Index of Contents

Introduction

Plastic production is continuously increasing. This is due to the unique properties of plastic materials such as low density, low thermal and low electric conductivity, resistance to corrosion, promising water/oxygen barrier properties, combined with a low price and an easiness in manufacturing [20]. Unfortunately, plastic materials are easily degradable due to their sensitivity against several factors such as UV radiations, water, fire, mechanical and frictional forces. This results in a progression of structural and chemical changes that induce the loss in mechanical integrity, embrittlement, further degradation and fragmentation [21].

When released in the ambient, small plastic fragments are particularly harmful as they can be easily ingested by living beings and hence enter in food chain [22], with a potential toxicity that has recently become relevant and attracted interest of the scientific community [23]. Plastic fragments with a dimension inferior to 5 mm are commonly called *microplastics* (MPs), even if this definition is still controversial. Furthermore, this definition also includes plastic fragments in the nano-size range, defined *nanoplastics* (NPs).

During the last decade, several studies have been conducted on this topic. These studies, whose results will be presented and analysed in the first part of this thesis work, demonstrated the applicability of various methods to remove MPs from aqueous environment. Nevertheless, one of the major drawbacks of these approaches, is their inefficiency in the removal of the smaller fraction of microplastics, known as nanoplastics.

The problem of plastics removal has also aroused interest in the legislative bodies. In particular, the idea behind these initiatives is to establish an emission limit in wastewater as already present for numerous other pollutants. In 2019, for instance, ECHA (European Chemical Agency) proposed to ban the use of MPs in cosmetic products and this should happen by 2030 [24]. At the same time, the World Health Organization is starting to study more deeply the possible consequences on MPs ingestion on human health [25].

It is important to highlight that the study of this form of pollution has long been complicated by the lack of an unambiguous and clear definition of microplastics, as explained in the first Chapter of this work. At the state of the art, the common definition of MPs is the one spread by The Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP). Microplastics are described as "*plastic particles < 5 mm in diameter, which include particles in the nano-size range*". Furthermore, MPs are commonly classified as primary or secondary, depending on their origin: primary ones are plastic parts in the micro-size range directly immitted in water, while secondary ones originate from the degradation of massive plastic components.

The main source of MPs into the environment is constituted by anthropogenic activities, both of industrial and domestic derivation, and several possible mitigation actions are currently under study.

The first possible mitigation action consists of processes which aim at reducing the number of MPs released in water by increasing the resistance of plastic fibres (see Chapter 2). Essentially, these methods are surface treatments and modification processes applied to textile fibres typically employed to produce clothes, one of the main sources of emissions.

Concerning the MP removal from water, the first tested methods were those that are nowadays industrially applied to the removal of solid particulates from wastewater to produce drinking water. These techniques are the subject of the third Chapter of this thesis work.

At the state of art, other research-level techniques have been tested. These can be classified according to their basic operating principle in chemical, physical, or biological methods, and are introduced in Chapters 4 to 6. Currently, no one of the techniques presented can solve the problem on MPs in water by itself. An integration of two or more techniques is mandatory to reach good removal efficiencies.

The purpose of this work is to provide a systematic description of the techniques currently available to limit or to avoid the emission of microplastics into the sea through wastewater, as well as to provide a research plan to develop a standard procedure for NPs sampling, analysis and removal. To this aim, a bibliographic research consulting scientific articles, conference proceedings and specialized internet sites was first carried out. The final objective is to present an overall and complete view of MPs issue, discussing both consolidated large-scale solutions and processes that are currently being tested at the lab scale only. The last part of this work, concerning the analysis and removal of NPs, aims at covering a current literature lack.

1 Microplastics Pollution

The increasing use of plastic materials in different industrial fields like food packaging or biomedical industry, is essentially due to their versatility and [26] unique characteristics such as low density, low thermal and low electric conductivity, resistance to corrosion, promising water/oxygen barrier properties, combined with a low price and an easiness in manufacturing [20]. As a consequence, the dispersion of plastic fragments and objects in the environment is constantly increasing, particularly in seas, with several consequences on the ecosystem [22].

Plastic materials are degradable due to their sensitivity against several factors such as UV radiations, water, fire, mechanical and frictional forces. This results in a progression of structural and chemical changes that induce the loss in mechanical integrity, embrittlement, further degradation and fragmentation [21]. When released in the ambient, small plastic fragments are particularly harmful as they can be easily ingested by living beings and hence enter in food chain [22], with a potential toxicity that has recently become relevant and attracted interest of the scientific community [23].

The aim of this Chapter is to define Microplastics and to describe their main sources, as well as providing a general overview of the degradation processes they undergo in marine environment.

1.1 Definition of microplastics: a controversial issue

Microplastics (MPs) are usually defined and classified according to their dimensions.

Traditionally, MPs have been described in function of an upper limit dimension as "*plastic particles smaller than 5 mm*" [20] [27]. This definition was reviewed several times in the last ten years and its usage still raises several issues.

At the current state, the common definition is the one spread by The Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP). Microplastics are described as "*plastic particles < 5 mm in diameter, which include particles in the nano-size range*" [20] [21] [28]. Nevertheless, some researchers still use as upper limit the dimension of 1 mm [27].

Consequently, the definition of *macro-* and *meso-plastic* follows. According to GESAMP [21], meso-plastics have a dimension < 2.5 cm and macro-plastics < 1 m.

The debate about the lower limit is surely more controversial. In fact, as reported by Dehaut et al. [27], a limit of 100 nm was established in correlation with the definition of nanomaterials.

The issue is that microplastics are not homogeneous in shape because of their different origin and chemical nature, which determines different behaviors in terms of aggregation and porosity [20] [27]. Moreover, it is important to highlight that in function of the size and of the shape of the particle, the effect on the ingestion mechanism by marine organisms is slightly different [29]. Therefore, the *shape factor* should be included in the definition [27]. The different possible shapes for MPs are reported in Figure 1.1.

Shape	Most common polymers
Granular	PE
Fiber	PES, PET, PA
Film	PP, PE, PA
Fragments	PP, PE, PET
Foam	PU, PVC, PS

Figure 1.1 *MPs possible shapes [11]*

According to other authors [20] also the color should be considered, and this is necessary especially for studies concerning aquatic organisms, as some species potentially ingest pollutants depending on a color preference.

In conclusion, it is evident that the current definition results restrictive. Therefore, several proposals of improvement have been recently suggested [27] even if these are not recognized by the entire scientific community.

1.2 Microplastics sources

The Scientific Community reported observations of plastic garbage in the oceans already in the early 1970s. More recently, it was noticed the presence of MPs litters in sand and in water [26].

The origin of these kinds of waste is complex to catalogue. A first classification is the following one [26] [21]:

a) Direct introduction (pellets, masterbatch pellets, textile fibres [21]). This kind of sources are reported in literature as *primary sources*.
b) Weathering breakdown of plastic debris of bigger dimensions (*meso-* and *macro*-plastics debris). This kind of sources are defined *secondary*.

The heterogeneous origin of MPs is also confirmed by their variety in colour. This aspect also confirms that they typically originate from synthetic materials and that may contain organic substances [23].

As reported in literature [21] [23], the main primary sources of MPs are constituted by plastic production waste, fragments originated during recycling operations and micro-cleansing particles in personal care products like facial scrubs.

Secondary MPs originate from larger plastic fragmentation: mainly from marine litter and synthetic fibers originating from laundry discharge; secondly from landfills and industrial or agricultural sources [26] [21] [23]. The identification of secondary MPs is complicated due to the large diversity of sources and pathways of degradation. In fact, fragmentation can be caused by mechanical forces, thermo-degradation, photolysis, thermo-oxidation and biodegradation processes [26] [22] [23].

One of the main MPs sources is constituted by the synthetic clothes washed inside the domestic washing machines. This is highlighted in Figure 1.2.

As reported by Julien Boucher and Damien Friot in their report for the IUCN (International Union for Conservation of Nature) [1], the global yearly consumption of fibres for fashion has increased over the last two decades (+79.3% between 1992 and 2010). This growth is almost exclusively due to the increased consumption of synthetic fibres with an increase close to 300% (from 16 to 42 million tons) over the same period. The majority (62.7%) of synthetic fibres are nowadays consumed in developing economies. The 35% of primary MPs discharged in water, come from synthetic textiles originating small fragments inside the washing machine.

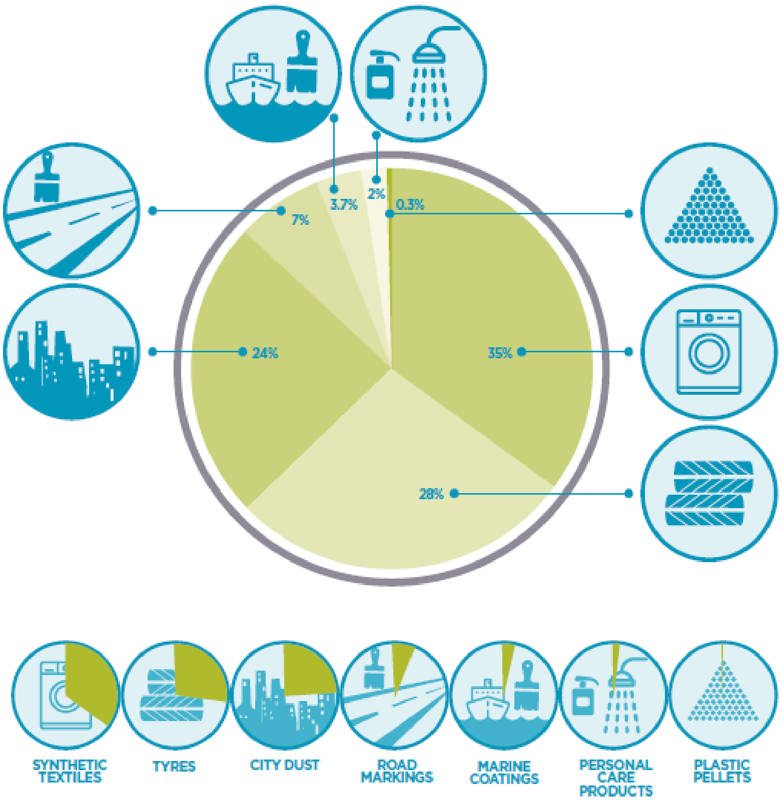


Figure 1.2 *Global Release of primary MPs to world oceans [1]*

It is interesting to notice that the spread of the COVID-19 pandemic has concretely increased the production of plastic waste and consequently of MPs. In particular, this is due to the necessity to produce Personal Protective Equipment for residents and healthcare staff and to the increase in the request of single-use packaging for food and groceries delivery [3]. In particular, single-use facemask degradation could be a new source of microplastic pollution in the environment. The long fibers used in masks can easily degrade, reaching the critical length of 5 mm [2].

In order to resume the main industrial sectors of MPs origin, Table 1.1 is reported.

1.3 Chemical Nature of Microplastics

MPs are polymeric materials. These are composed of long-chain molecules that are generated by the repetition of chemical structural units, the so-called *"mers"*.

Polymers are generally classified in two macro-categories: thermoset and thermoplastic ones.

The first class is made up of materials that cannot be processed at the molten state, as they have a network structure: by heating up this kind of materials they undergo a degradation process. On the other hand, thermoplastic ones can easily be melted, as they do not have a cross-linked structure.

As reported by A.L. Arandy [26] [28], the most common polymers found in MPs are thermoplastic ones: Polyethylene (PE), Polypropylene (PP), Poly-vinylchloride (PVC), Polystyrene (PS) and Poly-ethyleneterephthalate (PET).

Furthermore, fibers (mainly of Poliamide, PA) have been frequently sampled. These are typically obtained by a drawn process and are characterized by a very high level of crystallinity [28].

The presence of thermoset polymers is surely less common and not often discussed in literature. Researches have highlighted the existence of traces of Polyurethane foams, epoxy adhesives or paints, reinforced unsaturated polyester composites (GRP), and rubber. All these materials are used in the marine environment [28].

The densities range of most common polymers found in MPs is reported in Table 1.2.

Table 1.1 *Main origins for MPs. Adapted from ref. [2]*

Category	Source sector
Producers/ Converters	• Plastic Producers, Fabricators, Recyclers: Pellets and fragments
Sectoral consumers	• Agriculture: Greenhouse-sheets, pots, pipes, nutrient prills; • Fisheries: Fishing gear, packaging; • Aquaculture: Buoys, lines, nets, PVC pipes; • Construction: EPS, packaging; • Terrestrial transportation: Pellets, tyres, tyre dust; • Shipping/Offshore industry: Paints, pipes, clothes, miscellaneous, plastic-blasting, cargo; • Tourism industry: Consumer goods, packaging, microbeads, textile fibres; • Textile Industry: Fibres; • Sport: Synthetic turf.
Individual consumers	• Food and drink single-use packaging: Containers, plastic bags, bottles, caps, cups, plates, straws, spoons, etc. • Cosmetics and personal care products: Microbeads, packaging, toothbrushes, etc. • Textiles and clothing: Fibres.

Table 1.2 *Densities of most common polymers found in MPs. Adapted from ref. [7]*

Material	Density [g/cm^3]
Polyethylene (PE)	0.91-0.96
Polypropylene (PP)	0.90-0.91
Poly-vinylchloride (PVC)	1.16-1.55
Polystyrene (PS)	1.05
Poly-ethyleneterephthalate (PET)	1.37
Polyamide 66 (PA66)	1.14
Polyurethane (PU)	1.05-1.21

1.4 Plastic degradation mechanism in marine environment

Polymers degradation mechanisms are essentially four: photodegradation, thermo-oxidative degradation, hydrolytic degradation and biodegradation by microorganisms [22]. Degradation processes reduce the average molecular weight of the polymer, altering its structural properties, and change its chemical structure influencing its functional characteristics [26].

The degradation of polymers like LDPE (Low Density Polyethylene), HDPE (High Density Polyethylene), PP and nylons exposed to the marine environment, is generally driven by their interaction with ultraviolet (UV) light from the sun. UV radiation provides the activation energy required to initiate the oxidation of the polymers (*photo-oxidative degradation*) [26], which become brittle and start breaking in smaller parts [26] [22]. This point is critical because it leads to the formation of MPs, that can be ingested by marine microorganisms [26]. Once initiated, the degradation process can also proceed *thermo-oxidatively* for some time without further exposure to UV radiation [26].

After several fragmentation steps, polymer chains reach a sufficiently low molecular weight and dimension. At this point, plastic materials can be metabolized by microorganisms, who can convert the carbon in the polymer chains to carbon dioxide or incorporate them into biomolecules. This process is called *biodegradation* [22].

Nevertheless, in a marine environment, the latter process is several orders of magnitude slower compared to light-induced oxidative degradation of plastics [26]. This retardation is primarily the result of the relatively lower temperatures and of the lower oxygen concentration in seawater. The discrepancy in the degradation rates between air and sea is further accentuated by fouling effects due to the formation of a biofilm on the surface of plastic parts.

Moreover, hydrolysis is usually not a significant degradation mechanism in seawater [26].

1.5 Removal methods: summary of the state of art

During the last decade, several studies have been conducted on MPs removal from wastewater. This topic is very current and new studies have been recently published.

The main methods for MPs removal are introduced in the following chapters.

In particular, the first analyzed are essentially based on the application of well-known and widely diffused solid particulates removal techniques from drinking water or wastewater. In the subsequent chapters, research-level techniques are described and classified according to their basic operating principle: chemical, physical or biological methods.

2 Preventive and mitigation actions

The purpose of this first section is to describe the most recent ideas to prevent the emission of the primary MPs in water. As described in the previous chapter, this kind of pollutant mainly come from anthropogenic sources, both industrial and domestic and thus from consumer goods.

Unfortunately, considering that only recently a sensitivity towards this issue has developed, scientific researches on preventive actions are reserved to a few sectors of interest. In particular, this chapter will be focused on the strategies thought to reduce the production of plastic microfibers from clothes.

2.1 Surface treatments to prevent MPs fibers formation

One of the sources of primary microplastics in the ocean was identified in the washing of synthetic textiles. This was confirmed by the finding of MPs with the same proportions of polyester and acrylic fibers used in clothing in marine environment.

The release of microplastics from synthetic clothes during washing depends on several factors, such as fabric type, texture and yarn type. Furthermore, it depends on whether the fabric is made out of: staple fibers or continuous filaments, but also on the detergent used in the washing and on the washing conditions, such as temperature, mechanical action and water hardness [30, 31].

De Falco et al. [31] provided a quantitative analysis of the microfibers produced by three different synthetic fabric types: woven polyester, knitted polyester, and woven polypropylene during washing trials simulating domestic conditions. The highest release of MPs was recorded for the wash of woven polyester and this phenomenon was correlated to the fabric characteristics. Moreover, the number of MPs released from woven polyester fabrics due to different detergents, washing parameters and industrial washes was evaluated in the same study. The number of microfibers released from a typical 5 kg wash load of polyester fabrics was estimated to be over 6,000,000 in function of the type of detergent used. It was highlighted how the usage of a softener during washes reduces the number of microfibers released of more than 35%. Furthermore, regardless the type of fabric, the results indicated that powder detergent, higher temperature, higher water hardness and mechanical action increased the microplastics release. The electron microscopy (SEM) images of the samples showed that, considering dimension and size of the released microfibers, this kind of MPs could not be retained by the existing water treatment plant.

One of the possible surface treatments to mitigate the MPs production provides the use of pectin (structural formula is shown in Figure 2.1), a natural polysaccharide present in the cell walls of plants. To functionalize the fabric, pectin (PEC) was firstly modified with glycidyl methacrylate (GMA) and then grafted on polyamide [4]. It is important to highlight that pectin is cheap and abundantly available. In fact, it is a waste of fruit juice and sunflower oil production, and sugar manufacture. In the case of this study, pectin was extracted from suitable agro-by-products like citrus peel and apple pomace. One of the main drawbacks of pectin use is that it is soluble in aqueous medium, limiting its application in sectors where the contact with water can induce an undesirable solubilization of the macromolecule. To avoid this phenomenon, one possible solution is to mask its polar groups, such as carboxyl and hydroxyl, through their conversion into ester units.

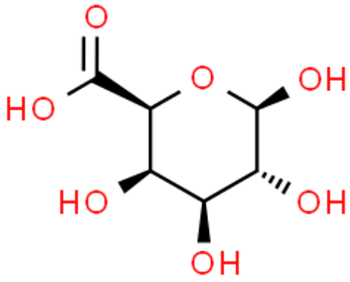


***Figure* 2.1** *Pectine Molecule (β-D-Galactopyranuronic acid) [32]*

In this study, masking was performed firstly modifying pectin with glycidyl methacrylate (GMA), showed in Figure 2.2. GMA was then grafted on the surface of polyamide fabric by cross linking reaction. The effectiveness of the treatment in reducing the MPs production from the fabric was tested and confirmed through washing trials simulations.

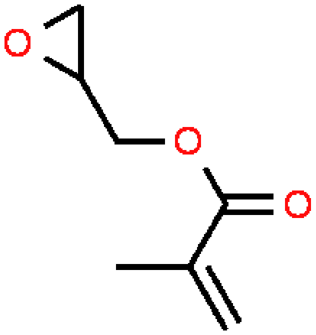


***Figure* 2.2** *Glycidyl methacrylate [33]*

Reactions involved are reported in Figure 2.3. In particular, the reaction responsible for the formation of the PEC-GMA product is a three-membered ring opening and a subsequent reaction with a carboxyl group of the pectin monomer through a nucleophilic substitution reaction. This kind of reaction, hiding the highly polar carboxyl groups, reduce the water solubility of pectin. Furthermore, the reaction PEC-GMA introduces vinyl groups in the polysaccharide structure, representing the reactive site for the grafting to polyamide during the second step. The grafting reaction occurs through a free radical polymerization, using sodium persulfate as initiator.

The surface of the structure PEC-GMA-PA was then analysed using SEM and some significative pictures are shown in Figure 2.4. The surface roughness results only slightly decreased so the appearance of the fabric is not modified, and this is an important feature considering the field of application of the fibres.

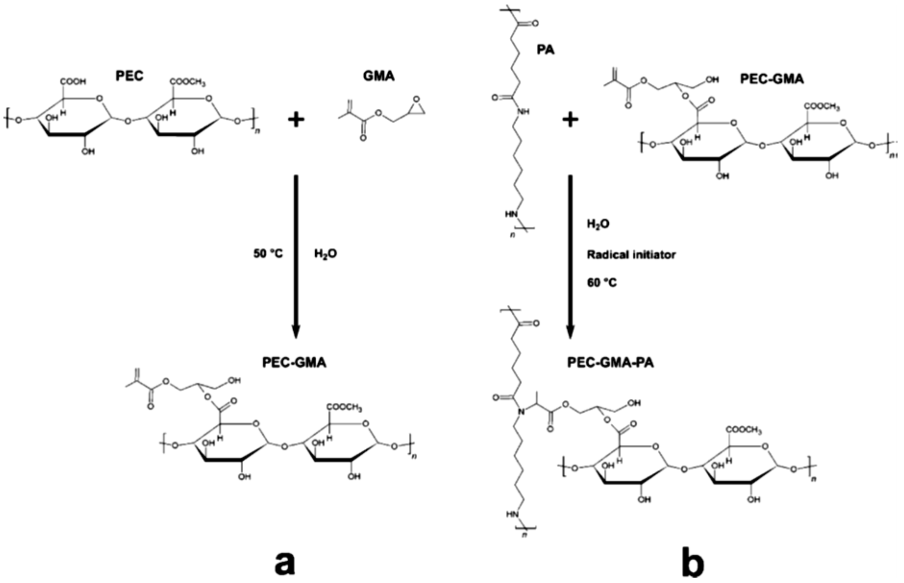


***Figure* 2.3** *Masking reaction schemes: (a) synthesis of PEC-GMA, (b) grafting of PEC-GMA on PA [4]*

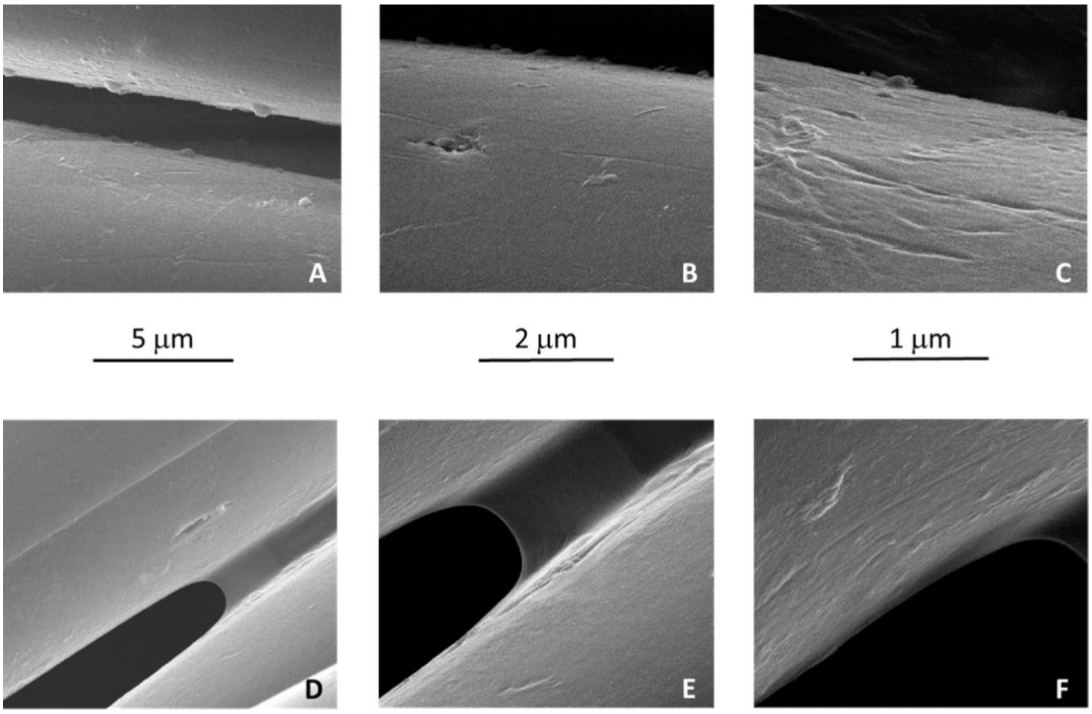


***Figure* 2.4** *SEM micrographs. A–C) PA surface and D–F) PEC-GMA-PA surface [4]*

Washing tests executed on the treated fabrics revealed that the treatment can reduce by almost 90% the number of MPs released.

Furthermore, this treatment is compatible with existing fabric production techniques. In fact, polyamide fabric was immersed in the reactive solution and then squeezed with a roll, simulating a padding process which basically consists of two steps. Firstly, the fabric is immersed in the liquid bath of substances to achieve a good impregnation and then it is passed between two rollers to squeeze it.

Afterwards, the same research team proposed another kind of surface treatment for polyamide fabrics [5], performed by an ElectroFluidoDynamic (EFD) method.

This approach was used to obtain homogeneous coatings of biodegradable polymers, namely poly(lactic-acid) (PLA) and poly(butylene succinate(PBS)-*co*-butylene adipate) (PBSA), on PA surface. PLA and PBS are shown in Figure 2.5 and Figure 2.6, respectively.

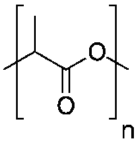


Figure 2.5 Molecular Structure of PLA [34]

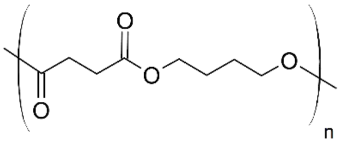


Figure 2.6 Molecular structure of PBS [35]

EFD is a versatile and cost-effective process, often used to functionalize polymer-based textile substrates. This promising technology is based on liquid atomization employing electrical forces. Due to these forces, the meniscus of a liquid flowing out a capillary nozzle elongates, forming a fine jet, which next is atomised into fine droplets. Depending on the flow rate and potential of the capillary, the droplets can be of submicron size, with narrow size distribution.

SEM micrographs of PA fabric, before and after the surface treatment are shown in Figure 2.7. The morphological analysis performed on the surfaces of PLA and PBSA coated polyamide samples was essential to confirm the effective presence of homogeneous and uniform coatings; furthermore, the surface of the coatings appears smooth and thin.

The effectiveness of the surface treatments in reducing the release of fibrous MPs during washing, was tested through washing tests at lab scale. A relevant reduction, of more than 80%, of the amount of microfibres released during washing tests of treated fabrics was obtained. Furthermore, the developed coatings proved to endure washing cycles, with PLA more durable than PBSA coatings showing a promising application as mitigation action of the environmental impact of synthetic textiles.

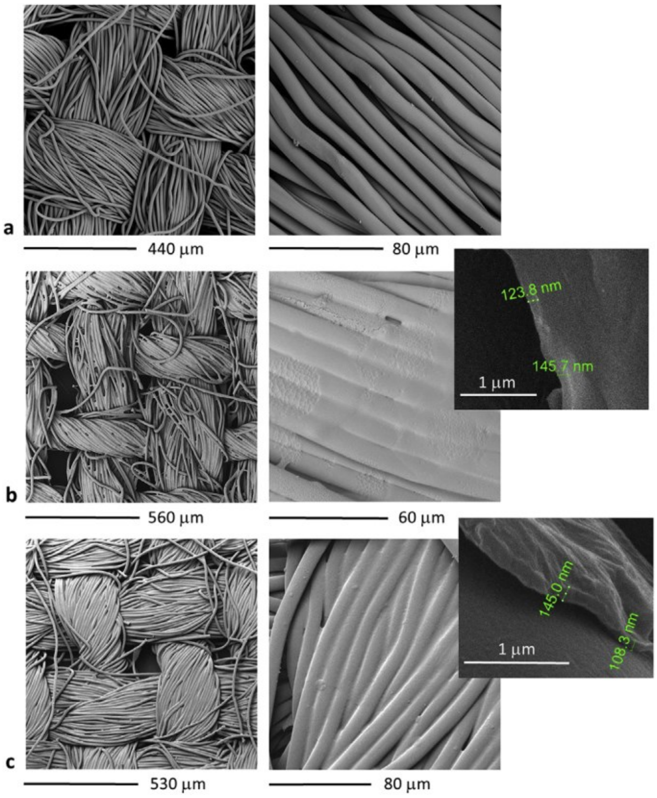


Figure 2.7 *SEM micrographs of polyamide fabrics, PA, a) neat; b) coated with PLA, c) coated with PBSA [5]*

2.2 Summary and conclusions

These techniques can be considered absolutely promising in preventing the production of primary MPs from clothes. The common point is trying to act before microfibers are produced during the washing cycles. As highlighted in this Chapter, using an adequate treatment, the production of MPs can decrease up to the 80% or 90%. These surface treatments have to be properly set and must avoid the use of more polluting substances. One limitation is the endurance time of these coatings onto the fabrics; these are progressively deteriorated by the washing processes because of heat, frictional forces and detergents.

Nevertheless, these treatments properly coupled with the removal actions introduced in the following chapters, could significantly contribute to the reduction of MPs emissions into seawater.

3 Methods based on solid particulates removal

The first studies conducted on MPs removal were essentially based on the same working principles used for water purification applied to solid particulates in wastewater plants (WWTPs) [36] or in drinking water treatment plants (WTPs) [11]. These studies essentially tested the already existent plants, sampling raw and treated water. One of the most controversial issue connected to this topic is the need for a standard procedure for MPs isolation, processing and identification in wastewater samples in order to obtain comparable and consistent results. Despite the lack of a standard procedure, several studies have been recently conducted and the obtained results have several common points. Beyond a quantitative analysis, different authors also proposed a qualitative analysis with the aim of identifying the main polymers present in MPs. These analyses are typically conducted through nondestructive spectroscopic techniques, such as Fourier transform infrared spectroscopy (FTIR) or μ-FTIR and Raman or μ-Raman spectroscopy [36].

These removal methods are presented in this Chapter, as well as the possible enhancement for the WWTPs and WTPs to adapt them for MPs removal.

3.1 Wastewater treatments applied to MPs removal

Wastewater treatment plants (WWTPs) are the primary receptors of MPs derived from anthropogenic activities, as sketched in Figure 3.1 [6].

The working principles of these plants are already consolidated for solid particulates removal coming from domestic and industrial wastewaters.

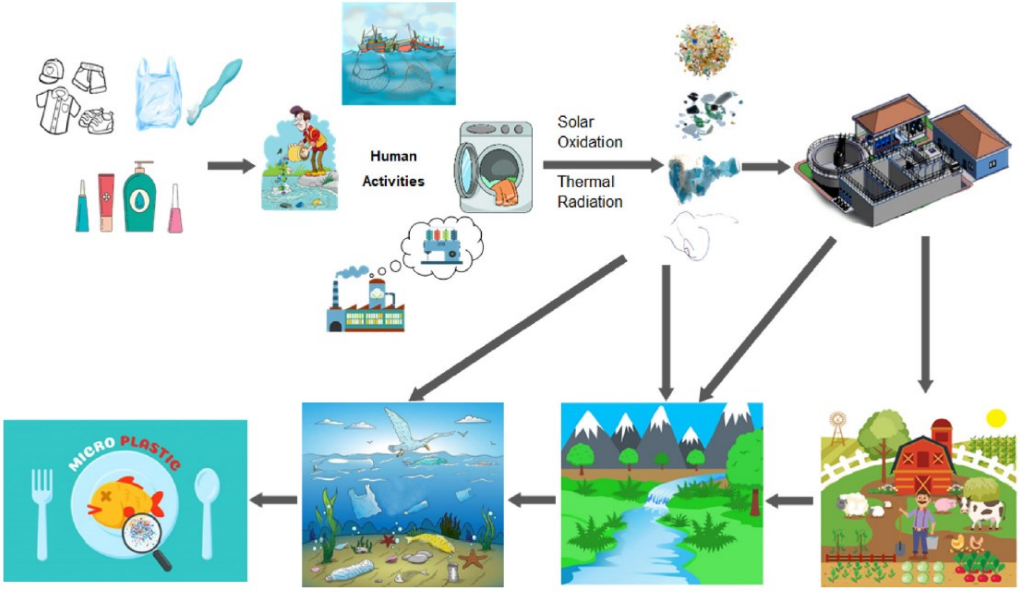


Figure 3.1 MPs fate in the ecosystem

The water treatment processes are generally organized in steps and each one has its own influence on the final removal rate [37]. In the following, a description of the possible technological approaches adopted for each removal step is presented.

Firstly, the inlet water is conducted to a grit chamber/primary sedimentation chamber. According to several studies conducted in different WWTPs, 40%-70% of MPs are removed at this level through a surface skimming and sedimentation process. In some WWTPs, around 90% of the MPs were removed. Such high removal efficiencies have been found in the literature when MPs have predominantly a fibrous morphology. Despite this step being quite effective in MPs removal, the following steps must be properly optimized in order to enhance the retaining capability of the considered WWTP [37].

One of the possible secondary process inside the WWTP is the Dissolved Air Flotation (DAF) which is designed to remove insoluble substances in water. During the DAF process, tiny bubbles are created by dissolving air into water at high pressure. These bubbles attach to the surface of suspended solids, resulting in the rising of solids and being removed by skimming. Recently, DAF has been found to offer high removal rates (95%) for MPs removal when their concentration in water is relatively low ($2 \pm 0.07\ MPs/L$).

Based on the literature reviews, coagulation process is often applied in the tertiary treatment stage by using chemical coagulants (ferric and aluminum salts or their derivatives) to destabilize surface charge and form flocs with MPs and other contaminants in wastewater and then remove them by settling or skimming. In general, the coagulation/flocculation process could help to remove up to 90% of MPs. The efficiencies reachable by this method are strongly influenced by the pH value. Other impacting factors are the size, shape and components of MPs as well as the dosage and type of coagulant and flocculant aids [37]. Nevertheless, the number of researches related to this technology for MPs removal is still limited, especially for wastewater treatment systems. More laboratory-level coagulation techniques are described in the following chapter of this work.

Following coagulation step, a filtration process is typically provided. Filtration can be obtained using different equipments. One of the most common possibilities is the use of a Sand Filter. This kind of system works according to a simple physical principle that consists in a capturing mechanism between sand grains or in an adhesion to the surface of sand grains. Removal rates can reach the 56%. Nevertheless, these values are obtained only when MPs are mainly in the shape of spheres, pellets and fibres. An evolution of Sand Filter technology is the Rapid Sand Filter (RFS), based on the same principles but made of different media layers. In this case, high removal rates are obtained when the MPs concentration is low. In recent years, also Granular Activated Carbon (GAC) was employed to filter emerging water pollutants like MPs. This technology is less effective compared to the traditional ones, with a removal rate of 60.9%. Disc Filters (DC) made up of large pores membranes ($10 - 20\ \mu m$) were also used but the corresponding efficiencies are typically lower because MPs adhesion to the membranes can induce fouling phenomena. Moreover, these filters are cleaned through a high-pressure backwashing process. Consequently, MPs can pass through the membrane and this reduces the overall removal rate of the system [37, 38].

Among the typical WWTP processes, the Conventional Activated Slug Process (CASP) has been evaluated for MPs removal. Briefly, this process consists in the biodegradation of MPs by an activated sludge which is then separated by a sedimentation tank. CASP has been largely used to treat soluble/colloidal organic pollutants and nutrients in many different types of wastewater. Nevertheless, the capability of CASP to decompose MPs is not proved by many studies and the published results are not in agreement with each other [37]. One of the main drawbacks of this technique is the production of excessive slug. This problem is partially solved by using Membrane Bioreactor (MBR), a combination of biology and membrane separation technologies. MBR is widely used for the removal of emerging pollutants (antibiotics, pesticides, personal care products, pharmaceuticals) and it has been recently studied also for MPs removal. In fact, MPs dimensions match the microfiltration membrane modules. Differently from other technologies described before, the performance of MBR seems to be not affected by the size, shape and composition of MPs [37, 38].

In recent years, ozonation was considered as an additional treatment step for the removal of emerging micropollutants from WWTPs effluents. This technology is promising also for MPs removal [37, 39]. Oxidation can break the polymers constituting MPs in smaller functional groups. The ozonization process is the direct reaction with molecular ozone and the indirect reaction of hydroxyl radicals (·OH) produced by the decomposition of ozone. Ozone reacts selectively with compounds containing electron-rich groups such as organic molecules. Dissolved organic matter is converted into smaller and structurally-related substances called *ozonation transformation products* that are commonly more biodegradable and less toxic.

One of the main emerging issue of WWTPs is that smaller particles are not easily retained by the treatment plants and thus pass through the process [40]. This is confirmed by several studies. For instance, Liu et al. [6] have investigated the MPS retaining capability of CASP, typically used in this kind of plants. Their work was focused on a WWTP in Wuhan City, China. This plant works according the flow chart reported in Figure 3.2 that also highlights the water sampling sites in this study. Specifically, these are the following ones, selected at four different stages of the treatment process: inlet of coarse grid (influent, identified as W1), outlet of the primary sedimentation tank (W2), outlet of secondary sedimentary tank (W3), and outlet of chlorination disinfection (effluent, marked as W4). Wastewater was sampled for three times (8:00, 13:00, and 18:00) at each sampling site. 10 L wastewater was poured into a sieve with a mesh size of 47 *μm* using a bucket made of stainless steel (twice each time), and MPs particles were washed thoroughly using pure water into glass bottles. Bottles were then placed at 4 °C until further process.

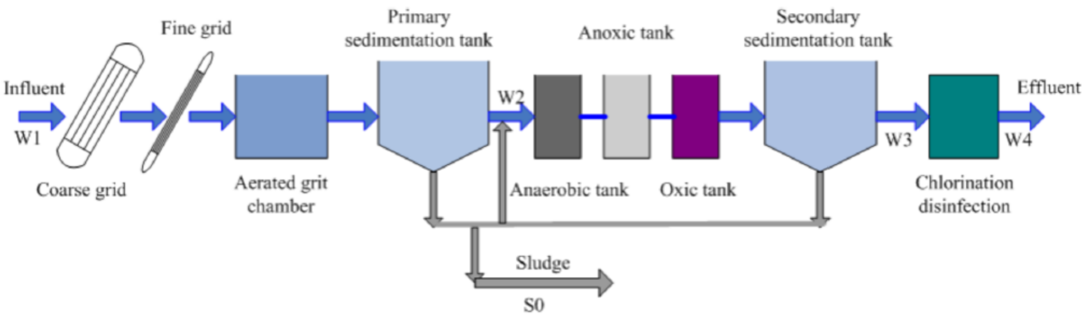


Figure 3.2 Overview of the WWTPs tested process [6]

Following an extraction process, MPs were observed and visually identified using a body fluorescence microscope. This operation was repeated for the samples collected at each step of the treatment.

Representative type of particles, observed with microscope in wastewater and sludge, were randomly selected and examined using micro-Raman spectroscopy to identify their structure and composition.

From the data collected, a series of conclusions were drawn. Concerning the abundance, it was found a value of $240.3 \pm 31.4\ MPs\ g^{-1}$ in the sludge with an average particle size of 0.22 mm. The larger size fraction of particles decreased through the different step (from W1 to W4), while the smaller ones were not retained. These results are resumed in Figure 3.3.

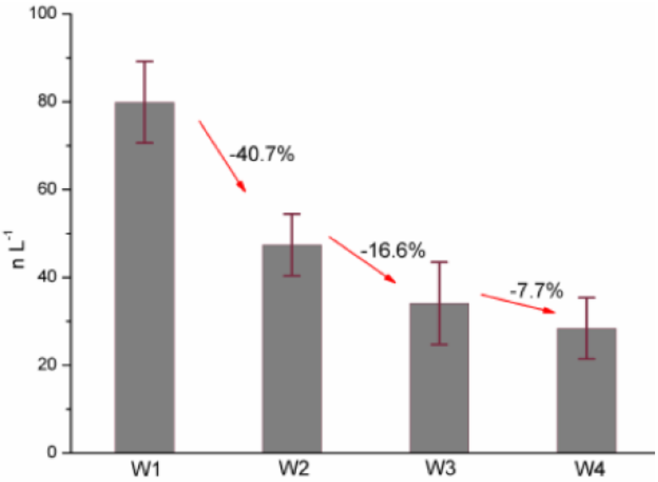


Figure 3.3 Abundance of MPs through the different steps of treatment [6]

Concerning the composition, PA was found to be the main polymer present in wastewater. This suggests that the MPs particles found in WWTPs are mainly originated from the wastewater discharged by washing clothes, considering that this material is often present in clothes composition. Therefore, the results of this study show that this WWTP is effective in decreasing MPs, even if smaller particles are discharged with the slugs.

Another point that deserves to be mentioned is the influence of the specific final stage of treatment (typically the tertiary stage) on the retention capability of the WWTP, that has been proven to strongly influence MPs retention. This topic was analyzed by several authors [38, 37] and the obtained results highlight that an advanced final-stage treatment can improve the MPs removal from the effluent. In 2015, Talvitie et al. [38] proposed a comparison between four WWTPs utilizing different advanced final-stage technologies. The study included membrane bioreactor (MBR) treating primary effluent and different tertiary treatment technologies (discfilter, rapid sand filtration and dissolved air flotation) treating secondary effluent. The results proved that with advanced final-stage technologies, WWTPs can substantially reduce the MPs discharged in marine environment. Furthermore, each of the advanced technologies proposed has a different removal rate. In particular, it was found that MBR removed 99.9% of MPs during the treatment (from 6.9 to 0.005 MPs L^{-1}), rapid sand filter 97% (from 0.7 to 0.02 MPs L^{-1}), dissolved air flotation 95% (from 2.0 to 0.1 MPs L^{-1}) and discfilter 40-98.5% (from 0.5-2.0 to 0.03-0.3 MPs L^{-1}). The sampling activity conducted showed that the treatments also removed all size fractions and shapes of MPs, as shown in Figure 3.4. It is important to notice that the smallest size fraction ($20 - 100\ \mu m$) and textile fibers were the most common types before and after the final treatment. This highlights the need for final-stage technologies to remove small size and fiber-like MPs from effluents that are not easily removed with a typical WWTP. Concerning the chemical nature of MPs, FTIR analysis revealed that samples were made of 13 different polymers, with the majority of PET and PE.

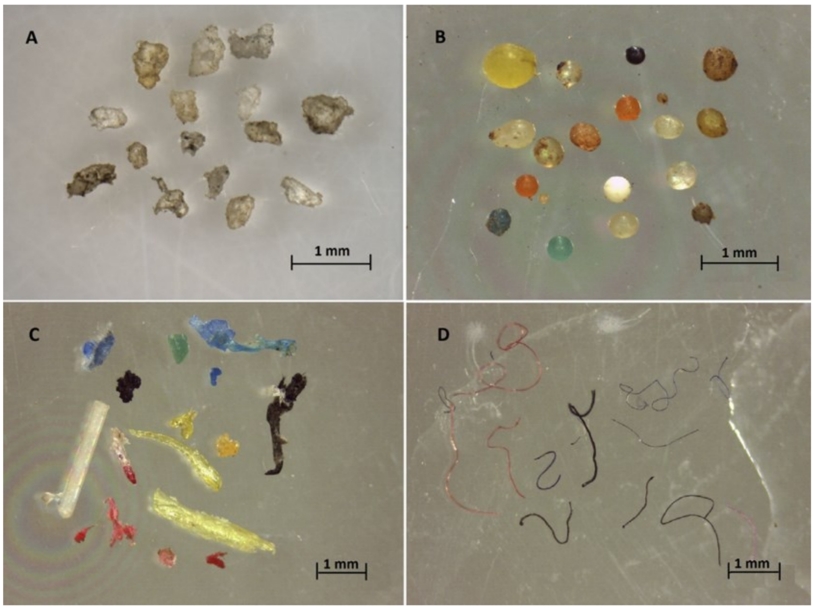


Figure 3.4 *Panel A and B: primary MPs. Panel C and D: Secondary MPs, fragments from break-down of larger plastics and synthetic textile fibers [38]*

3.2 Drinking water treatment for MPs removal

As reported by Shen et al., MPs and suspended solid particulates present similar physical properties. This justifies the possible use of traditional drinking water treatments for MPs removal. The latter generally includes coagulation, sedimentation, sand filtration and clarification [11].

Drinking water is a possible source of ingestion of MPs. As shown in Figure 3.5, plants treating drinking water are typically fed by rivers in turn polluted by the presence of MPs originating from anthropogenic activities.

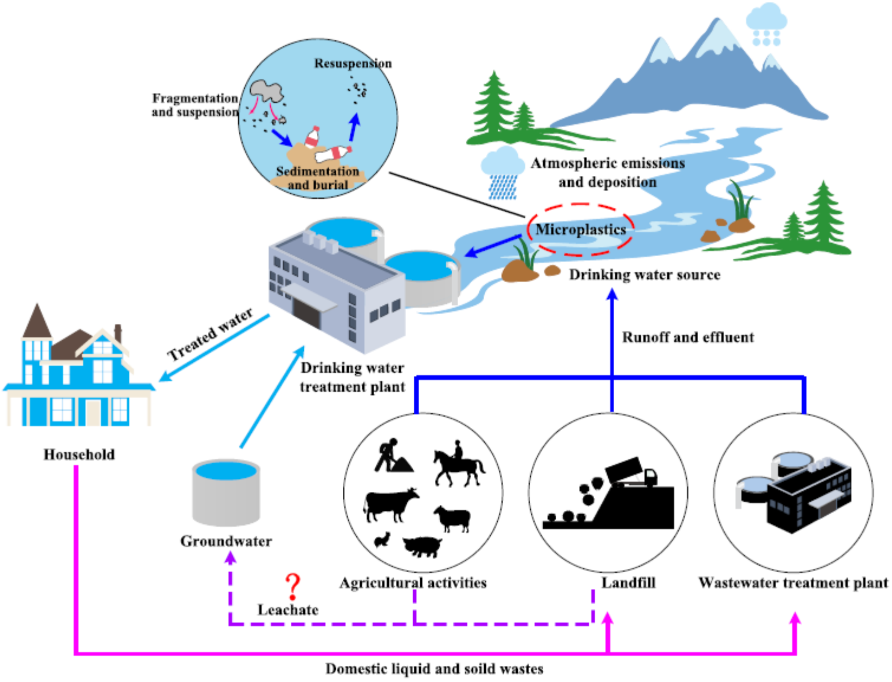


Figure 3.5 Sources and transport of microplastics in raw water and treated drinking water (tap water or bottled water) [11].

Pivokonsky et al. quantified and compared MPs content in raw and treated drinking water to provide a size classification of the particles and to identify prevalent morphologies, as well as to analyse the material composition [40]. Raw and treated water were sampled in three different plants (WTP1, WTP2, WTP3) in Czech Republic, working by using different technologies. WTPs characteristics are presented in Table 3.1.

It was found that the content of microplastics was significantly lower in treated compared to raw water (by 83% on average). Nevertheless, MPs concentration in treated water was not negligible, ranging from 338 ± 76 to $628 \pm 28\, MPs\, L^{-1}$. Concerning the dimension, the smallest particles were least retained. This was confirmed by the size range of the unretained MPs: up to 95% were within the size range of 1–10 μm. Most of the microplastics were composed of PET and PP in case of WTP1 and WTP2, and of PET, PP and PE for WTP3.

Table 3.1 *WTPs characteristics*

	Usual/ Maximum Capacity	Supplied Inhabitants	Technologies
WTP1	3700/7000 L s^{-1}	1.5 million	Coagulation/flocculation and sand filtration
WTP2	100/200 L s^{-1}	60 thousand	Coagulation/flocculation, sedimentation, sand and granular activated carbon filtration are operated
WTP3	90/150 L s^{-1}	130 thousand	Coagulation-flocculation, flotation, sand filtration and granular activated carbon filtration

3.3 Summary and perspectives

Traditional treatment processes, both for wastewater and drinking water, are promising for MPs removal and have inspired several laboratory-level researches. As demonstrated [38], the use of an advanced final stage of treatment can improve the efficiency of the plant in removing MPs from discharge water.

At the state of art, there is a lack of standard procedures for collecting and analysing MPs. Sampling is not a simple task, due to the particle's size and to the plastic composition. In fact, plastic materials are obtained by the combination of virgin polymers with fillers and additives. These latter may create difficulties in polymer type identification. Other problems that may emerge are bulking and foaming or a low sludge separability [36]. Despite these issues, several studies have been recently carried out and the obtained results have the following common points:

- Smaller MPs ($1-10\mu m$ or up to 100 μm if a tertiary advanced treatment stage is not provided) are not easily retained by the already existing treatment plants;
- Chemical analysis revealed that the most common polymers present in MPs are PET, PP, PE and PA, often with a fibrous morphology;
- A tertiary stage of treatment (coagulation, sand filter, RFS, GAC, DC, CASP, MBR, ozonation) is necessary to achieve high MPs removal rates.

It is evident that several other points are needed to be investigated. In particular, the microplastic particle size distribution in raw water, only obtainable through an accurate statistical analysis, and the interaction among MPs and other water pollutants.

In the next chapters, the main experimental laboratory-level techniques are introduced and divided as a function of their basic physical working principle.

4 Chemical Methods

Water treatment plants have shown several limitations in MPs removing. Consequently, new ideas and technologies are necessary to mitigate the phenomena. These innovative techniques are mainly developed on lab-scale and are based on different working principles.

This Chapter introduces the main chemical methods tested for MPs removal from water. Most of these techniques are essentially based on chemical or electrochemical reactions inducing agglomeration of the MPs in the aqueous system [41]. One of the main drawbacks of these processes is the potential environmental impact of the used reactants that is discussed in the sequent paragraphs.

Another process recently tested and presented in this chapter consists of the photocatalysis-induced degradation of polymers constituting MPs.

4.1 Introduction to the chemical principles applied

Most of the chemical processes applied to MPs removal are based on the sol-gel approach. This kind of process was observed for the first time in 1846 and was used to obtain SiO_2 from liquid, colorless tetraethoxysilane (TEOS) [8]. At the state of art, the sol-gel method is mainly appreciated for the synthesis of ceramic materials, metal oxides in particular. As it can be observed in Figure 4.1, the sol-gel synthesis involves the formation of a particle network and originates several products. The network created by the reaction itself can serve as a trap for microplastics.

Briefly, the sol-gel process starts from the synthesis of colloidal solutions (sol) which constitute the precursors for the subsequent formation of a gel, i.e. a continuous inorganic lattice containing an interconnected liquid phase, through hydrolysis and condensation reactions. For example, the sol-gel preparation of SiO_2 consists in a room-temperature hydrolytic polycondensation of silicon alkoxides liquid precursors under controlled conditions. The synthesis is generally carried out in an organic cosolvent (alkoxysilanes are not water-soluble), through simultaneous or sequential reactions of hydrolysis (eq. 4.1) and polycondensation, releasing water (eq. 4.2) and/or alcohol (eq. 4.3) [42].

$$\equiv Si - OR + H_2O \rightleftharpoons \equiv Si - OH + R - OH \tag{4.1}$$

$$\equiv Si - OH + HO - Si \equiv \rightleftharpoons \equiv Si - O - Si \equiv + H_2O \tag{4.2}$$

$$\equiv Si - OR + HO - Si \equiv \rightleftharpoons \equiv Si - O - Si \equiv + R - OH \tag{4.3}$$

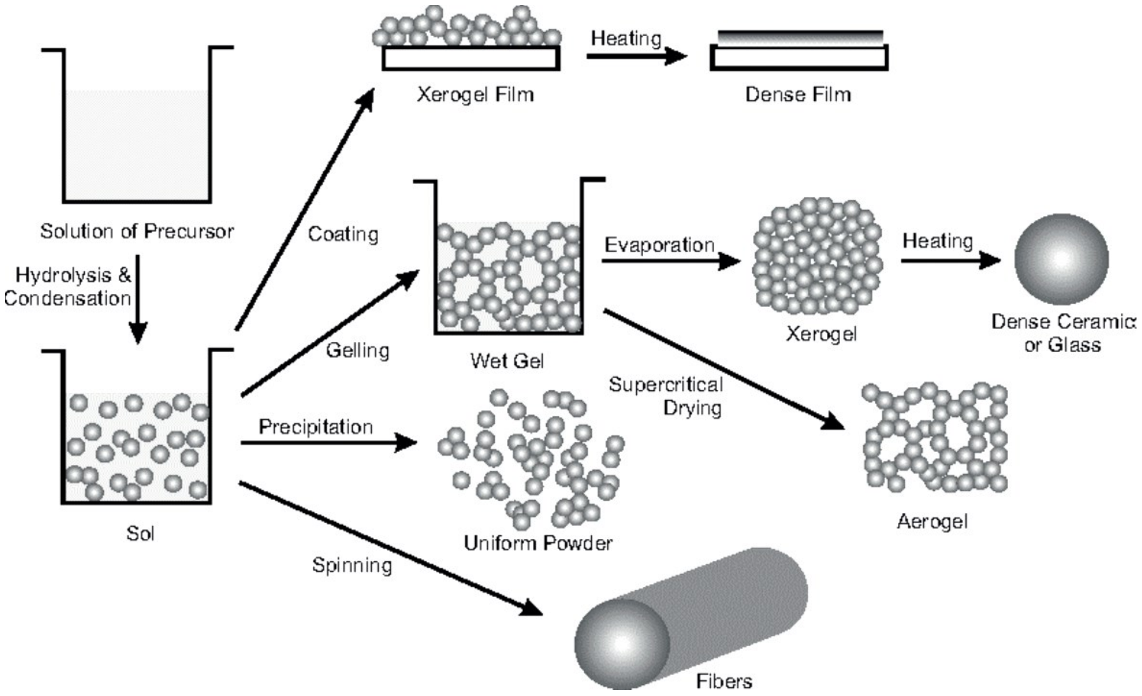


***Figure 4.1** Schematic overview of sol-gel processes [43]*

The macroscopic properties of the reaction products, such as porosity, specific surface area as well as the degree and manner of cross-linking are significantly influenced by the monomer silanes used in the sol–gel process and by the reaction conditions, such as pH value in the sol, molar Si–H_2O ration, type and concentration of the solvent and temperature. Aggregation and condensation processes are promoted by weak intermolecular forces (e.g. hydrogen bridge bonds, dipole–dipole interactions, etc.) [8, 42]. The mechanism differs depending on the type of the catalyst used: acids (H^+), bases (OH^-), or nucleophilic agents (F^-, N^-, methylimidazole, etc.) [8].

Several post thermal treatments are then typically performed to eliminate the liquid phase from the gel and to improve the mechanical properties of the final products.

4.2 Coagulation for MPs removal

4.2.1 Coagulation induced with a sol-gel process

As described in the previous paragraph, the formation of a particle network is implicit in sol-gel processes. This network can serve as a trap for MPs dispersed in water. Plastic particles are attracted by weak intermolecular forces to the gelling particles and hence their volume is increased. The increase of volume is helpful in removing processes. In fact, the traditional water treatment plants have several limitations in retaining smaller particles, while bigger MPs could be more easily retained.

In 2018, Herbort et. al tested the effectiveness of this phenomena using bio-inspired alkoxysilanes as precursors [8]. This work was based on the idea that short-range Van der Waals interactions as well as hydrophobic interactions between precursors and/or material and chemical-inert polymers constituting MPs can induce particle growth.

Hence, through the addition of adequate sol-gel reaction precursors, it is possible to begin a molecular self-organization in water. This results in an *adhesion particle*, growth around the polymers particles and between the precursors molecules, as well as between the particles themselves. The agglomerated clusters obtained can then be separated from the aquatic media through a simpler filtration process.

The chemical substances used in this study to obtain the molecular precursors follow:

- 1,2-Dimethoxyethane;
- 3-Aminopropyltriethoxysilane;
- 3-Ureidopropyltrimethoxysilane (97%);
- Acetone;
- Ally bromide;
- Ammoniumfluoride;
- Ascorbic acid;
- Dichloromethane;
- Ethanol;
- Hydrochloric acid;
- *N*,*N*,*N*,*N*-tetramethylmethylenediamine;
- Potassium carbonate;
- Sodium hydroxide;
- Terephtalic acid (98%);
- Terephthaloyl dichloride;
- Triethoxysilane.

Several tests were done with different composition for precursors. The trapping of MPs was proved through ESEM and IR analysis on the samples obtained. In conclusion, the data confirm that it is possible to agglomerate, include, and remove inert organic chemical molecules, such as MPs from wastewater. Briefly resuming the overall process, bioinspired alkoxy-silyl, functionalized molecules act as adhesion reagents between the MPs particles. Through a sol–gel process, an agglomerate is formed. This corresponds to 666 times the volume of the original particle and subsequently can be removed through a traditional separation technique, such as sand filter.

Figure 4.2, obtained through an ESEM analysis, reports one example of agglomerate obtained with this approach. This figure also resumes the overall process.

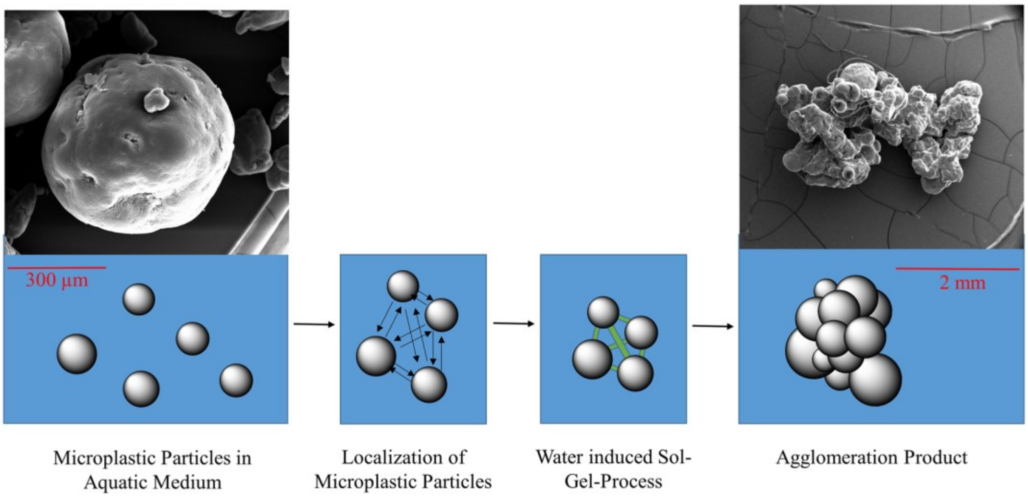


Figure 4.2 Resume of the process tested by Herbort et al. [8]

4.2.2 *Coagulation induced by salts*

Aluminium and iron salts are widely used as coagulants in water treatment. Al- and Fe- based salts were used as coagulants by Baiwen et al. [10, 9] in the presence of polyethylene (PE), which has a density similar to water (0.92–0.97 g/cm^3) and thus it is typically suspended in water. The chemical reagents used were the following:

- $AlCl_3 \cdot 6H_2O$;
- $FeCl_3 \cdot 6H_2O$;
- HCl;
- NaOH;
- $NaHCO_3$;
- Polyacrylamide (PAM)
- Kaolin.

Both Al(III) and Fe(III) have limited solubility at around neutral pH conditions and tend to precipitate in flocs.

Briefly, the process can be resumed as follows (Figure 4.3). Aluminium or iron salts are added to a suspension of PE in water. Destabilizing the system, for example by changing the pH of the solution or the concentration of salts, a coagulation of solid particles is promoted. MPs are trapped inside these salt agglomerates and therefore this increase in weight leads to sedimentation and precipitation of salts-MPs aggregates. Lowering the pH (for example with an anionic salt, such as anionic PAM), this phenomenon is exacerbated. A step of ultrafiltration and then of disinfection follow. In this way drinking water results purified.

The characteristic of flocs plays an important role in removing PE particles during coagulation. In particular, it was shown that Al-based salts performed better than Fe-based salts in PE removal. Several factors influenced the result. For example, the smaller the PE particle size, the higher the removal efficiency. Nevertheless, removal efficiency was quite low (40%) even with high aluminium salts concentrations. Additionally, water conditions, such as ionic strength and turbidity level, barely influenced the removal efficiency. One of the main influencing factors was the addition of polyacrylamide (PAM), especially in its anionic form. Its addition determines the generation of positive-charged Al flocs.

For ultrafiltration, although PE particles can be completely rejected, slight membrane fouling was induced after coagulation with conventional Al-based salts. With increasing dosage, membrane fouling was gradually aggravated owing to the thick cake layer formed. However, the larger the PE particles, the greater the roughness of the Al-based floc cake layer, leading to less severe membrane fouling. Based on this investigation, the MPs removal behaviours exhibited during coagulation and ultrafiltration processes have potential application in drinking water treatment.

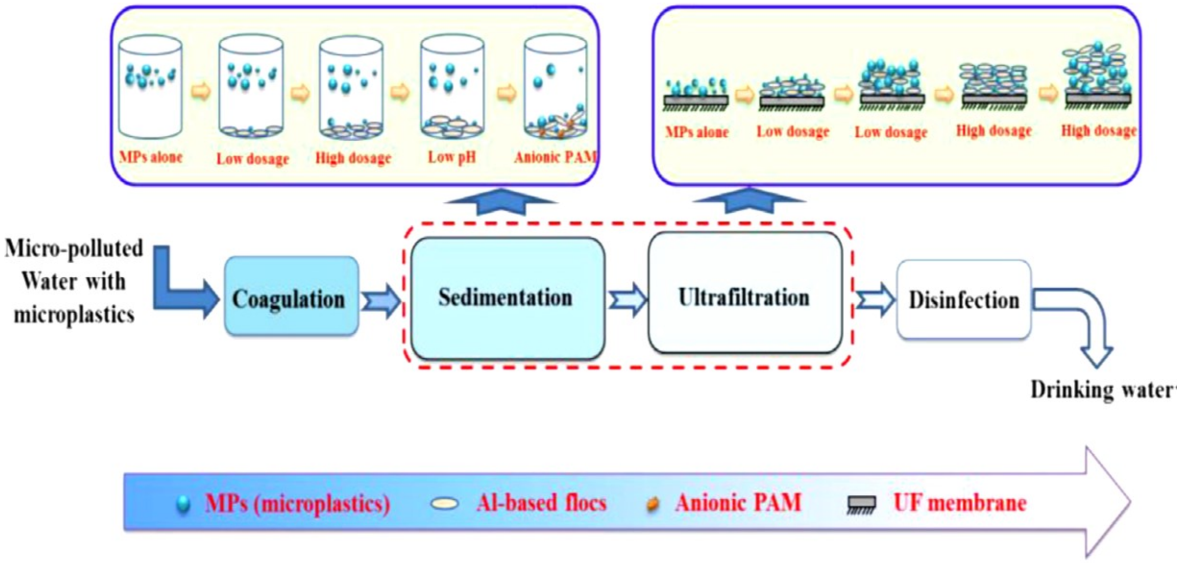


Figure 4.3 Salt induced coagulation process scheme [10]

Skaf et al. tested *alum* as another possible coagulants [44]. An alum is a type of chemical compound, usually a hydrated double sulphate salt of aluminium with the general formula $XAl(SO_4)_2·12H_2O$, where X is a monovalent cation such as potassium or ammonium. Generally, the name "alum" refers to aluminium sulphate $Al_2(SO_4)_3·nH_2O$, which is used for most industrial flocculation. [45].

The results of this work confirm that conditions which are suitable for the removal of kaolin are also effective for the removal of a model plastic sphere (density 1.3 g/cm^3, 1–5 μm diameter). Coagulation using alum at concentrations between 5 and 10 mg/L significantly reduced water turbidity. Evidently, MPs precipitated. Evidences from floc photos and zeta potential measurements, indicate that flocculation is the dominant mechanism for microsphere removal in the conditions of this study. The same test was repeated also for fibrous MPs. The dispersion of polyethylene microfibers (density 0.96 g/cm^3, 5 μm diameter cut to 0.1 mm lengths) in water was strongly influenced by surfactants yet the fibres were still effectively removed via coagulation.

All the studies presented were conducted on lab-scale. Therefore, all these techniques should be coupled to the industrial plants for water treatments, in order to obtain realistic data on their efficiencies. Moreover, further experimentation with other plastics and solution conditions is needed to enhance the results.

4.3 An evolution of coagulation processes: electrocoagulation

Electrocoagulation is an environmentally friendly water treatment technique. In fact, metal electrodes are used to electrically produce coagulants; thereby, coagulation process results simpler and more automatable [11].

This process is briefly described below. First, under the action of an external electric field, metal ions (generally Fe^{3+} or Al^{3+}) are generated from sacrificial electrodes and enter in water stream. Simultaneously, these cations can recombine with hydroxiles groups in water, forming metallic hydroxides. The anodic (eq. 4.4-4.5) and cathodic (eq. 4.6-4.7) reactions are reported.

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^{-} \tag{3.4}$$

$$2H_2O_{(l)} \rightarrow 4H^{+}_{(aq)} + O_2 + 4e^{-} \tag{3.5}$$

$$M^{n+}_{(aq)} + ne^{-} \rightarrow M_s \tag{3.6}$$

$$2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-} \tag{3.7}$$

$$M^{n+}_{(aq)} + nOH^{-} \rightarrow M(OH)_{n(s)} \tag{3.8}$$

These compounds act as *micro-coagulants* inside the system. These coagulants destabilize the surface charge of the suspended solids, breaking up the colloid or emulsion, which in turn allows them to approach each other close enough for Van der Waals forces to take effect. This way, the coagulants form a sludge blanket, which traps the suspended solid particles. Therefore, suspended substances and colloidal pollutants in water lose their stability under the action of these coagulants. After an external destabilization of the system, pollutants and coagulants collide each other and micro-flocs are formed [11, 46]. The entire process is reported in Figure 4.4.

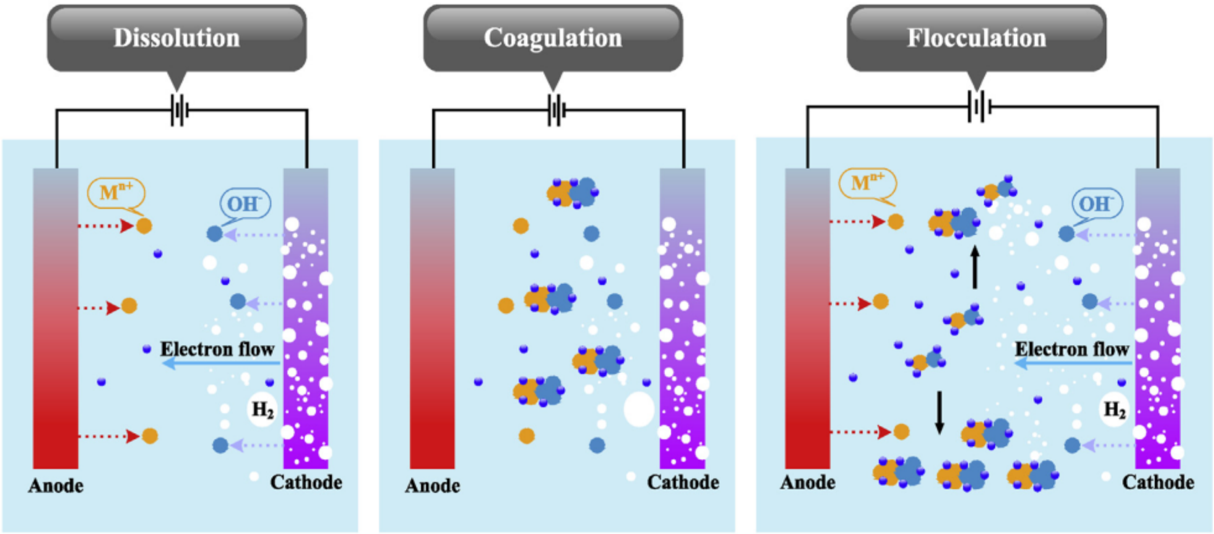


Figure 4.4 Electrocoagulation process [11]

This technique has been widely used for the removal of pollutants other than MPs. Two of the main advantages of this technique are that sludges are minimized, and it is energetically efficient.

In 2018, Perren et al. [46] adapted this process to the removal of PE beads. The process is showed in Figure 4.5.

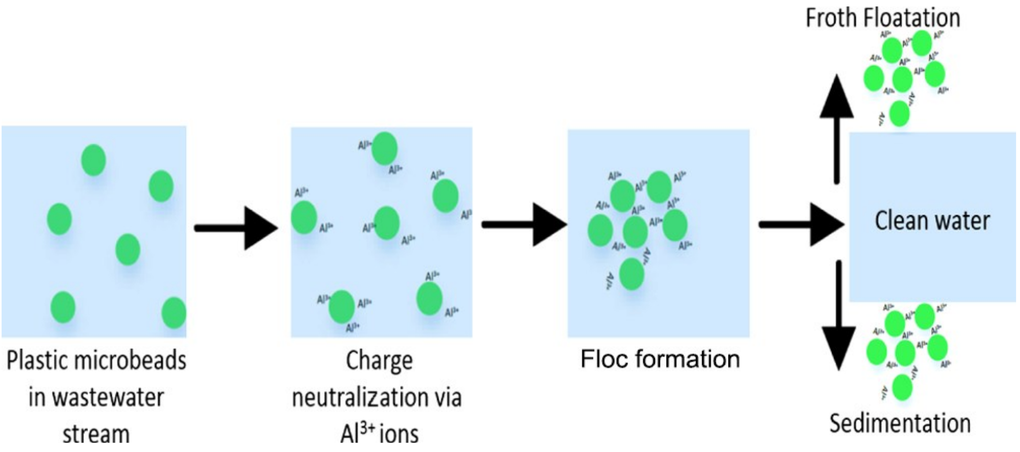


Figure 4.5 Elecrocoagulation for PE beads removal [46]

The removal efficiencies obtained were all in the range 90-100%, even changing the operational conditions considered. These conditions were initial pH, conductivity (evaluated as NaCl concentration) and current density. Observations showed that microbeads underwent both flocculation and charge neutralization simultaneously. The optimum working conditions for the reactor to emphasize both the phenomena (flocculation and charge neutralization) are resumed in the following Table 4.1.

Table 4.1 *Set of operative condition required to emphasize both flocculation and charge neutralization*

pH	7,5
NaCl concentration	2 g/L
Current density	11 A/m^2

In the same article, it was speculated that on large scale the most suitable option of an EC cell to removing microbeads should be a two stage, continuous EC reactor/settler unit. Nevertheless, further research should investigate possible reactor designs and configurations to optimize the process.

4.4 Photocatalysis: a degradative process for MPs treatment

Another approach for MPs removal is based on a degradative process induced by photocatalysis. Through degradation, polymers are converted in less polluting substances.

Briefly, photocatalytic degradation occurs when a semiconductor is exposed to a source of light emitting photons with equal or higher energy than its band gap, generating holes (h^+) and excited electrons (e^-). These holes, combined with water (H_2O) or hydroxyl groups (OH^-), generate hydroxyl radicals ($OH\bullet$) which are highly oxidizing species capable of degrading many organic pollutants, generating different chemical substances.

Ariza-Tarazona et al. [12] tested the efficacy of N-TiO_2 as a semiconductor to degrade HDPE extracted from a commercially available scrub, showed in Figure 4.6.

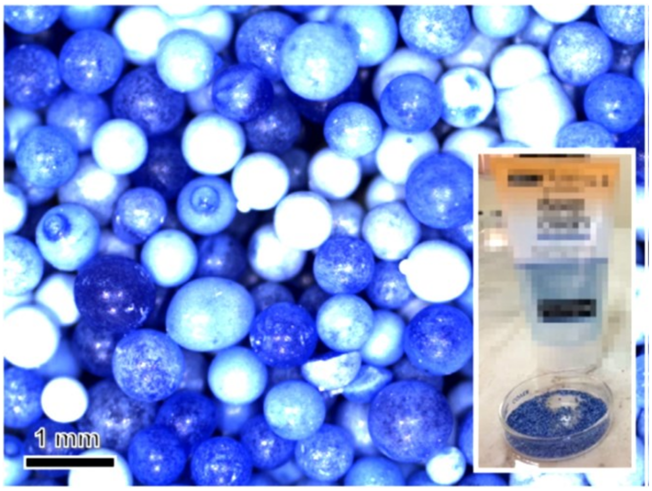


Figure 4.6 *Optic micrograph of the extracted microplastics (16 ×) [12]*

To achieve a more sustainable process, the semiconductor was obtained by a bio-inspired synthesis process using mussel proteins as pore-forming agent and nitrogen as source for the photocatalyst doping. The same test was repeated with a N-TiO_2 obtained through a traditional sol-gel synthesis. The photocatalytic experiments performed with the mussel-derived N-TiO_2 powders were carried using microplastics/N-TiO_2 film composites, reported in Figure 4.7. Plastic degradation was measured by weight loss, with chemical and morphological changes confirmed by FTIR and SEM. A second photocatalytic test was conducted using the HDPE/N-TiO_2 composite in an aqueous medium at room temperature.

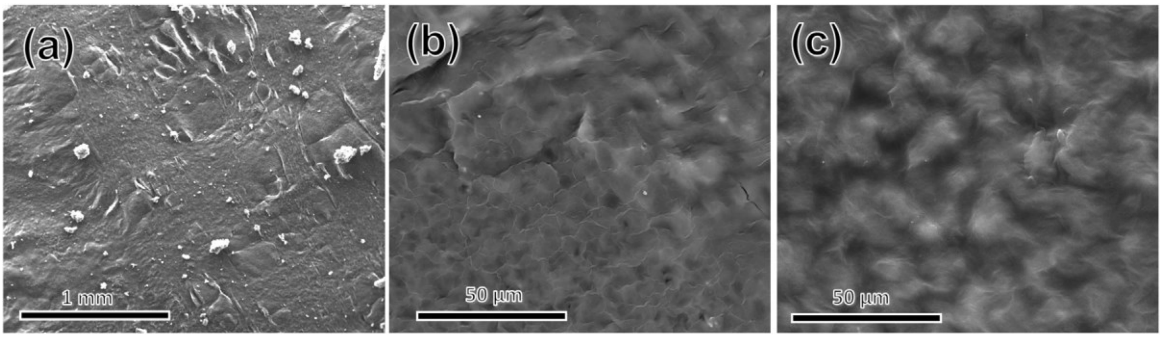


Figure 4.7 *SEM micrographs of the HDPE/N-TiO_2 composites (semiconductor derived from the proteins). (a) As-prepared, (b) solid photocatalysis and (c) aqueous photocatalysis [12].*

It was concluded that the more sustainable N-TiO_2, derived from saltwater mussels, presented an excellent capacity to promote mass loss of HDPE microplastics in the solid and aqueous environment. The other photocatalyst, derived from a conventional less sustainable sol-gel route, also presented good capacity to promote mass loss of the as-extracted microplastics in an aqueous environment. Results showed that the environmental conditions should be carefully set or designed in order of avoiding the arrest of photocatalysis.

Nevertheless, this process was only tested on lab scale and thus should be adapted for wastewater treatment plants.

4.5 Case Study: an innovative equipment for washing machines to reduce MPs emissions

One of the main MPs sources is constituted by the synthetic clothes washed inside the domestic washing machines.

This issue has started attracting companies' interest and of the household appliances producers in particular. In 2019, Rold an Italian company producing components for washing machines, launched a challenge for the students from Politecnico di Torino: realizing a functional prototype for an innovative equipment to mitigate the emission of MPs in water.

One of the solutions proposed[6] was an agglomeration process, using eco-friendly chemical agents. The designed equipment (showed in Figure 4.8) was constituted by two sections, the first one (physical-mechanical) responsible of the interception of the microfibers, and the second one (chemical) dedicated to the treatment of the retained particles to obtain a handily big solid agglomerate that can be easily disposed of. The interception of microfibers is performed with a micrometric filter, made of a synthetic fabric. The backwash process of the filter, feasible thanks to a proper renovation of the hydraulic configuration of the washing machine, concentrates the microfibers in a small amount of water simplifying the chemical treatment. This consists in a sort of *gellification* of the polluted water up to reach a quite solidification. The substances involved, both reactants and products, are eco-compatible and safe, not irritating or corrosive. Hence, problems related to their use should be limited, both for humans and environmental impact.

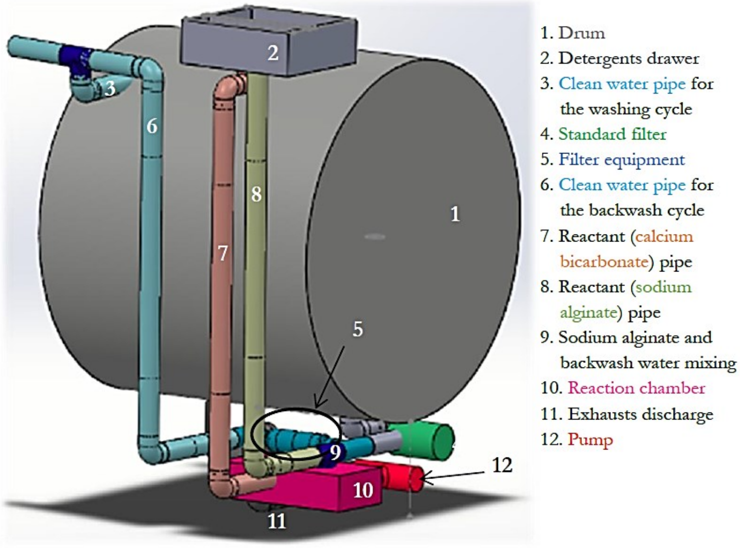


Figure 4.8 *Team Bold Designed Equipment*

Considering the entire washing-machine system, there are three filters:

- The standard filter of the washing machine;
- The pre-filter, with a bigger mesh size, compared to the microplastics one, and necessary to create an intermediate step of filtration, preventing a faster filling of the micro-scaled filter;
- The micro-scaled filter, which is the core of the system, necessary to trap the microplastics and increase their concentration in water.

One of the most challenging aspects of this work is that the density of the dispersed fibres is very similar to the water's one. Moreover, the various microfabrics produced

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[6] Team Bold, composed by: Romina Arena, Melania Fiore, Sofia Izzi, Simone Martini, Leonardo Sergio, Sergio Salvatore

by clothes are chemically different, so it is not possible to use gravity or specific system's properties, as pH or temperature gradients, to separate them or induce their aggregation. For this reason, it is worthwhile acting with chemical reactants to promote aggregation of particles and hence to facilitate their removal, taking advantage of the dimension increase.

As already discussed, Herbort et al. [8] , proposed a new lab-scale approach to remove polymers from aquatic systems by using sol-gel induced agglomeration reactions to form larger particles. In this way, the agglomeration can be carried out completely independently of the type, size and amount of the substance concentration as well as of the external influences, like the already mentioned ones, pH value, temperature or pressure. The idea is basically adding the chemical precursors for sol-gel synthesis as if they are some detergents, which directly reach the reaction section. The sol-gel synthesis consists of two steps: hydrolysis and condensation, during which precursors form big networks that trap microfibers and create larger particles.

Nevertheless, one of the main issues of the sol-gel reaction is related to the environmental impact of the precursors typically used for the sol-gel synthesis, like the alkoxy-silanes proposed by Herbort et al. [8].

Hence, similar processes to obtain bigger particles using less-impacting substances were studied. The idea was to use a jellification process inspired to the molecular kitchen, the so-called *spherification*. This simple process is used to obtain "fake caviar", made for example of roses or strawberries syrup [47]. Considering the edible applications, the substances involved are certainly human-friendly and the environmental impact should be quite low.

The spherification process consists of a first reaction between sodium bicarbonate and alginic acid, resulting in a suspension of sodium alginate which then reacts with calcium chloride: in this way gel particles are formed [48].

Alginic acid, $(C_6H_8O_6)_n$, is a hydrophilic and viscous polysaccharide present in algae, which form a gum when hydrated. Its structural formula is shown in the following Figure 4.9.

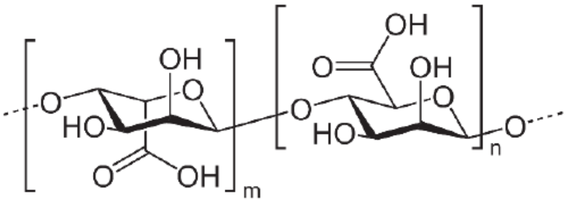

Figure 4.9 Structural Formula of Alginic Acid [49]

Sodium bicarbonate, $NaHCO_3$, commonly known as baking soda, is widely used for domestic purposes. It is a salt composed of a sodium cation (Na^+) and a bicarbonate anion (HCO_3^-).

As described, these two chemical substances react, forming sodium alginate, $(NaC_6H_7O_6)_n$, which is at solid state in normal conditions, in granular or powdered forms; its structure is reported in Figure 4.10.

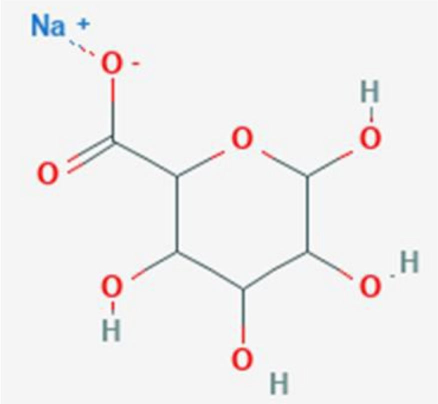

Figure 4.10 Structural Formula of Sodium Aliginate [50]

Calcium chloride, $CaCl_2$, which makes the spherification process possible, is an ionic compound of calcium and chlorine, highly soluble in water.

What is effectively performed with this process is an ionic-exchange process between sodium –bonded with alginic acid molecules – and calcium. Because calcium has a double charge compared to sodium, it can coordinate two alginate molecules. It is a polymerization process which occurs instantly when calcium chloride is added. The process is summarized in the Figure 4.11.

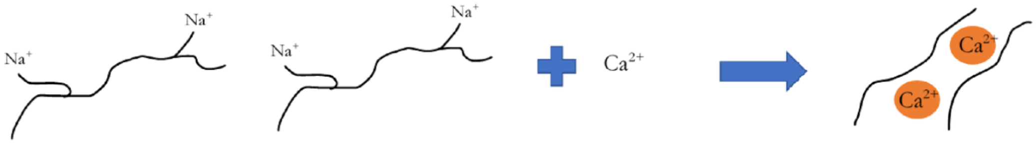

Figure 4.11 Working principle of the agglomeration process

The idea is that microfibers should be attracted by Van der Waals forces to these molecules during the reaction and therefore incorporated in the forming molecules. In this way, the disposal should be simpler, more efficient and user-friendly.

One of the main problems of this reaction is the use of calcium chloride because it is very corrosive and hence it compromises the functionality of the washing machine and of all the pipelines. Moreover, its emission limits in discharge water should be considered. Considering that the overall process is an ionic-exchange reaction, theoretically it can occur in the same way with other bi-valent salts to coordinate two molecules of sodium alginate.

In any case, various experiments were performed using the original reactants, sodium alginate and calcium chloride, in order to evaluate the reachable levels of solidification. For this purpose, several combinations in terms of the number of reactants and precipitation techniques were tested.

One example of aggregate obtained is showed in Figure 4.12.

Figure 4.12 *Example of aggregates obtained*

The results are surely promising, demonstrating that an eco-friendly aggregation process is feasible. Nevertheless, this was only a proof-of-principle study. Many more experiments are needed to evaluate the quantity of reactants and their best combinations.

4.6 Summary and perspectives

In this Chapter, several MPs removal techniques based on chemical processes were presented.

Although very different from each other, these all share the fact that they have only been tested on a laboratory scale. In the future, such processes should be integrated into domestic or industrial water treatment plants to improve them. All these techniques, however, are very promising and reach high removal rates.

A point to be evaluated in further studies is the environmental sustainability of the substances envisaged in the treatments and the consequences that their emission into the sea would have.

5 Physical Methods

The category of physical removing methods is wide and includes techniques very different from each other. These can be classified according to their specific working principle, which includes magnetic extraction, adsorption processes, or filtration/ ultrafiltration mechanisms as discussed in the following paragraphs.

These techniques, as well as the chemical methods introduced in the previous chapter, have been mainly tested on lab-scale. Filtration and ultrafiltration technologies have, in part, already been tested in industrial water treatment plants (WWTPs and WTPs) as described in Chapter 1 and reported here for completeness.

5.1 Functionalizing MPs for magnetic extraction

Plastic particles are generally characterized by a hydrophobic surface. Taking advantage of this peculiarity, Grbic et al. [13] used hydrophobic iron (Fe) nanoparticles that once bonded to MPs particles, allow a magnetic recovery. The procedure is sketched in Figure 5.1 and can be described as following.

The first step concerned the *hydrophobization* of Fe nanoparticles. This was obtained by a surface modification approach, anchoring to the surface Fe nanoparticles silane functional groups with hydrophobic hydrocarbon tails. Fe nanoparticles were chosen for their high surface area to volume ratio, low cost, and ferromagnetic properties. The tests were conducted on MPs samples with different size ranges: large (from $\sim 1\ to\ \sim 8\ mm$), medium (from $200\ \mu m\ to\ 1\ mm$), and small ($< 20\ \mu m$),. Moreover, their removal efficiency has been verified in different aqueous media (seawater or treated freshwater).

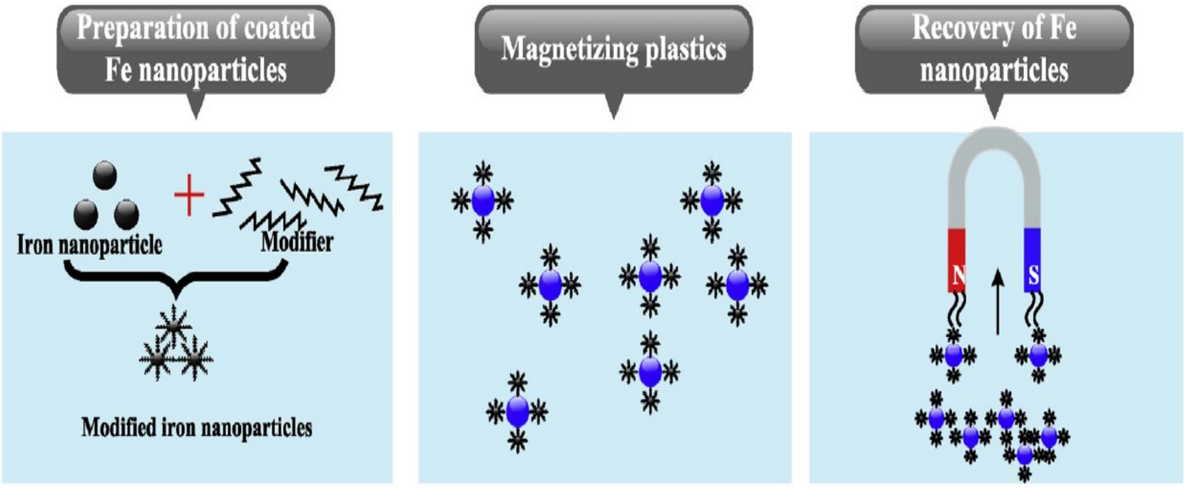

Figure 5.1 Process of Magnetic Extraction [11]

The results of this study showed a recovery rate of 92% for 10–20 μm polyethylene and polystyrene beads, and 93% for MPs >1 mm (polyethylene, polyethylene terephthalate, polystyrene, polyurethane, polyvinyl chloride, and polypropylene) from seawater. Furthermore, also the 84% and 78% of MPs (polyethylene, polystyrene, polyurethane, polyvinyl chloride, and polypropylene) ranging from 200 μm to 1 mm from freshwater and sediments were removed, respectively. Overall, this study demonstrated that the procedure is efficient for various sizes, polymer types, and sample matrices and it can be considered as a working step of the extraction procedure of MPs. A photograph of large MPs exposed to modified Fe nanoparticles is shown in Figure 5.2.

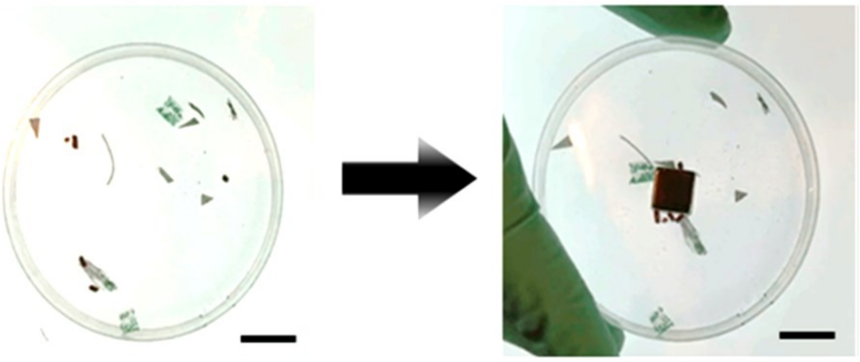

Figure 5.2 *Photograph of large MPs exposed to modified Fe nanoparticles being attracted to a magnet at the centre of the dish [13].*

5.2 Membrane technologies for MPs physical removal

Membrane technology has the advantage of a stable effluent quality and well-known operations. Depending on the membrane porosity and on the pressures applied, membrane separation technologies can be classified into ultrafiltration (1–100 nm, 1–10 bar), nanofiltration (1-2 nm, pressure up to 50 bar) and reverse osmosis (0,1-1 nm, 10–100 bar). The principle of membrane separation technology for water purification is shown in Figure 5.3. Simplifying, under the action of pressure difference, the pore size of membrane is used to intercept particles from raw waters [11, 15].

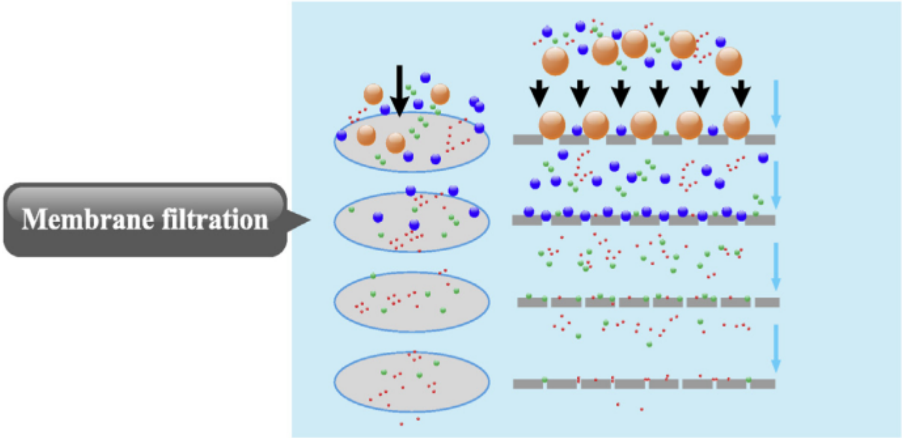

Figure 5.3 *Membrane filtration technology [11]*

The application of membrane technology for the removal of microplastics is still quite limited. Nevertheless, the last years registered an increase of studies about membrane separation processes and membrane bioreactors (MBR), often combined with other processes to reach higher removal rates [15]. The removal of MPs was found to strictly depend on some influencing factors that are briefly reported in Table 5.1.

Filtration and ultrafiltration membrane technologies are already widely used in waste and drinking water treatment plants to remove suspended solids and thus have partially already be presented in Chapter 2. However, these have only recently been used or tested on lab-scale also for MPs removal.

Table 5.1 *Influencing factors and membrane process parameters to be considered for MPs removal. Adapted from [15]*

	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 • Polarization concentration • Cake layer formation and fouling • Rejection/Removal • Specific energy consumption
Micro-Nanoplastic	• Shape • Size • Mass • Chemical composition • Concentration	

5.2.1 *Ultrafiltration Technology*

Ultrafiltration (UF) technologies are already used in wastewater treatment plants to remove organic substances such as proteins, fatty acids, bacteria, protozoa, viruses, and suspended solids. These techniques allow to obtain high quality drinking water in an economic way. This process is characterized by a low energy consumption, a high separation efficiency, and the plants are typically not space-occupying. It is a low-pressure process (1–10 bar) that uses asymmetric UF membranes having a pore size between 1–100 nm [15].

Nevertheless, these technologies are not properly designed for MPs removal. One possibility is to couple this process with a coagulation step. This hypothesis has been tested in 2019 by Ma et al. [10, 9] and the results were promising, as described in Paragraph 3.2.2.

5.2.2 *Dynamic Membrane Technology*

Dynamic membrane (DM) is emerging as an attractive process for wastewater treatment. This technology is based on the formation of a cake layer, i.e. the dynamic membrane, which acts as a secondary membrane/barrier created when particles and other foulants in the wastewater are filtered through a supporting membrane. The DM formation process depends on various parameters related to the supporting membranes (membrane materials, membrane pore size), to the deposited material (particle size, concentration) and to the operating conditions (operating pressure, cross-flow velocity) [15]. Dynamic membranes are a promising technology for the removal of low-density, non-degradable micro-particles, such as plastics [51].

In 2018, Li et al. [51] tested the effectiveness of DM technology for the removal of solid particles suspended in a synthetic wastewater. These particles were in the size-range of MPs, thus the results obtained could be used to speculate a similar treatment process also for MPs removal.

The effectiveness of the process was demonstrated through a turbidity measurement in NTU (Nephelometric Turbidity Unit), which is a way to determine the concentration of suspended particulates in a liquid or gas colloid. The instrument used for this measurement is called *nephelometer* or *turbidimeter*. A nephelometer measures suspended particulates by employing a light beam (source beam) and a light detector set to one side (often 90°) of the source beam. Particle density is then a function of the light reflected into the detector from the particles.

The main results are reported in Figure 5.4: it can be seen as the turbidity determined by a certain particle size distribution (left side of the picture) decreases in time when a DM process is applied (right side of the picture).

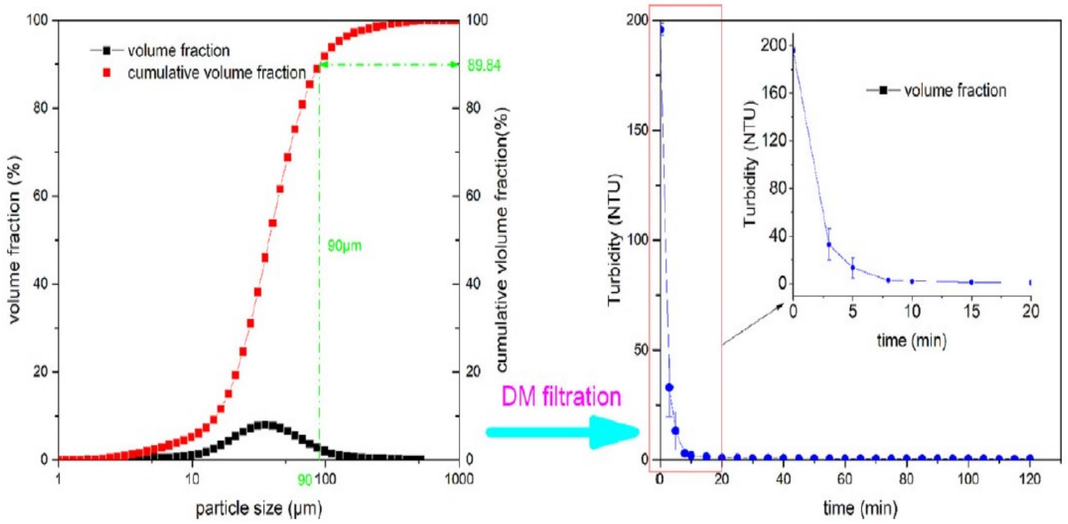

Figure 5.4 Effectiveness of DM process proved by a turbidity measurement [51]

5.2.3 *Reverse Osmosis*

Reverse Osmosis (RO) is used in industrial water treatment systems. These processes typically use nonporous or nanofiltration membranes (pore size <2 nm) for the removal of salts, contaminants, heavy metals, and other impurities. The application of a high pressure (10-100 bar) to a concentrated water solution forces the water through a semipermeable membrane, leaving all the contaminants in a more concentrated water solution [15].

This kind of process is currently applied in many industrial fields such as beverage production, biopharmaceutical manufacturing, power generation, production of high purity water, and desalination of seawater [15].

The effectiveness of this technology for MPs removal from discharge water has been tested by Ziajahromi et al. [52]. In particular, this research aimed at testing technologies already used in wastewater treatment plants. It was noticed that RO is quite effective in MPs removing compared to other technologies in addition to the other primary, secondary and tertiary stages of treatments, already discussed in Chapter 1. One of the most interesting samples analysed was taken from a WWTP in Sidney which produces highly treated effluent by applying primary, secondary and tertiary treatment processes. The latter include screening (mesh size of 3 mm) and sedimentation, biological treatment, flocculation, disinfection/de-chlorination processes, ultrafiltration, reverse osmosis (RO) and de-carbonation. The results obtained are graphically resumed in Figure 5.5.

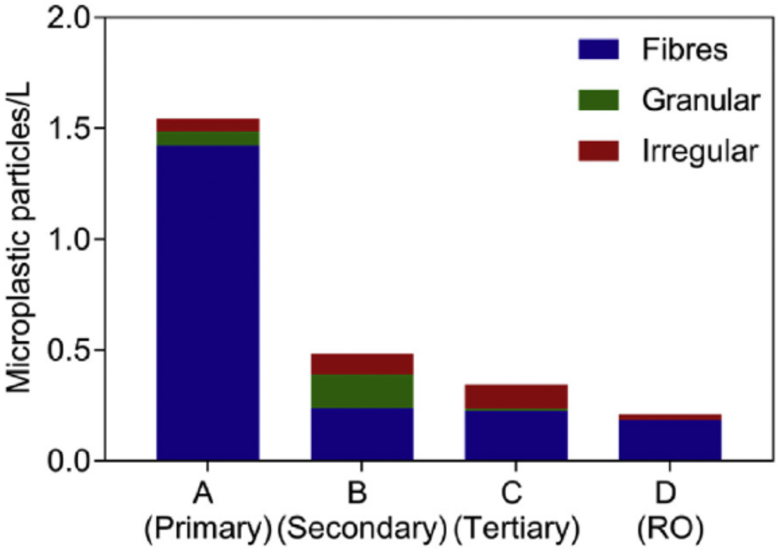

Figure 5.5 *Concentration of MPs in treated water after each step of treatment [52]*

5.2.4 Membrane Bioreactors (MBR)

The use of MBR technology in WWTPs and WTPs has been described in Chapter 1. Nevertheless, the peculiarities of this kind of system deserve to be deepened. MBRs are systems in which catalytic reactions promoted by biological catalysts, such as bacteria and enzymes, is coupled to a separation process, operated by a membrane system to promote microfiltration (100-1000 nm, pressures up to 5 bar) or ultrafiltration.

MBR process is shown in Figure 5.6. The membrane creates different compartments and consequently a controlled heterogeneous (organic/water)/multiphase (liquid/gas) reaction system can be developed. The different phases can be kept separated (as for example, in a membrane-based solvent extraction process), or they can be dispersed into each other (as in a membrane emulsification process) [15].

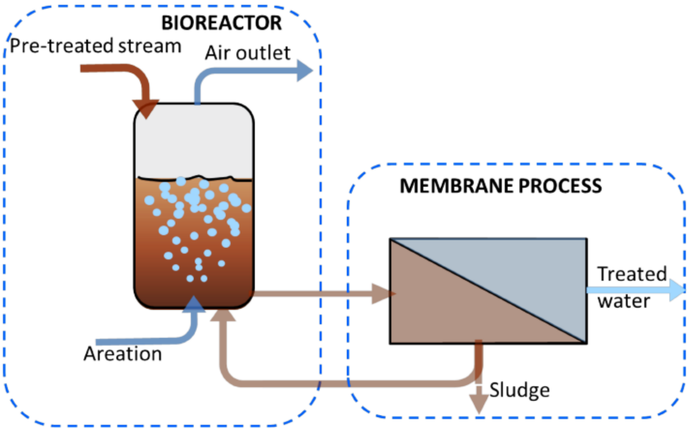

Figure 5.6 *MBR process [15]*

Specifically concerning MPs removal, the process generally starts when a pre-treated stream enters in the bioreactor, promoting a process of biodegradation of organic matter. The produced mixed liquor is then pumped along with semi-crossflow filtration system for the separation process (Figure 5.6). The membrane process concentrates MPs in the retentate stream.

The effectiveness of this method was recently evaluated for MPs treatment and the results were promising. Bayo et al. [14] obtained a removal efficiency of 79.01%, demonstrating the need for this kind of process in WTTPs after primary and secondary stages.

Specifically, more information about biodegradation and removal biodegradation-based techniques will be provided in Chapter 5.

5.3 Materials for MPs adsorption

MPs are characterized by a large surface/volume ratio and this makes the adsorption of other contaminants likely [53]. At the same time, MPs can be adsorbed by marine biota. This can be critical because potential seafoods are compromised but, at the same time, this property opens to the possibility of creating specific bio-inspired nanostructured adsorbent materials for MPs to improve the retaining capability of the treatment plants.

For instance, a study on the PS-adsorption capacity of an edible macroalga (seaweed), called *fucus vesiculosus,* was recently conducted. PS particles were observed on macroalga's surface after exposure to microplastic dispersions, with an average of 2.63 PS particles per mm. This result highlights a high degree of adherence of PS particles close to the cut surface, where MPs are trapped in alginate [16].

Arossa et al. [17] focused on the retaining capability of *Tridacna maxima*, a giant clam (Figure 5.7) characterized by a complex external surface.

These findings lay the basis for further studies to be conducted using other species, in order to better understand the interactions between 3D structure of organisms and microplastics.

Figure 5.7 *Example of giant Clam and of its surface complexity [53]*

Also, steam-activated pine and spruce bark biochar have been investigated as *bio-based* adsorbents for MPs [18]. Biochar samples were produced from the bark of scots pine by conventional slow pyrolysis at 475 °C and were steam-activated at 800 °C as shown in Figure 5.8. Steam activation is a relatively inexpensive method for creating porous biochar adsorbents from the bark-containing waste of the wood refining industry.

Figure 5.8 *The sample grid of the slow pyrolysis/activation reactor [18]*

The investigated parameters were phenol and MPs retention and cation exchange capacity. After the adsorption step, biochar samples were washed to evaluate the actual retaining capacity. The results for the different samples are resumed in Table 5.2.

Table 5.2 *MP material that could not be removed from the activated biochars by washing*

Sample	**Retention**
Pine bark AC, 30% steam activation	0.165 -0.096 g
Pine bark AC, 40% steam activation	0.130-0.040 g
Spruce bark AC, 40% steam activation	0.293- 0.046 g

The tested activated biochars efficiently removed the larger microplastics particles. However, the removal of 10 μm spherical microplastics was not acceptable, but the experimental results indicated that higher meso-and macropore contents could be beneficial for the removal of the smallest MP particles. In conclusion, steam activation is a suitable method for activated biochar production as it allows the obtainment of surface areas in the range of 400–600 m^2/g that are adequate for a good removal of contaminants from wastewater. Nevertheless, MPs removal using biochar requires further research, particularly regarding the recovery of smallest particle fractions.

Sun et al. [19] tested the effectiveness of a robust and compressive sponge prepared from chitin and graphene oxide (ChGO). Such sponges efficiently adsorbed different types of MPs from water at pH 6–8 and can be reusable. The adsorption capacity is 89.8%, 72.4%, and 88.9% for polystyrene (PS), carboxylate-modified polystyrene (PS-COOH), and amine-modified polystyrene (PS-NH2), respectively. The adsorption kinetic study suggested that the main driving forces for MPs absorption are electrostatic interactions, hydrogen bond interactions, and $\pi-\pi$ interactions. Furthermore, the intra-particle diffusion had a significant role in the whole adsorption process. Three cycles of adsorption-desorption were executed, as shown in Figure 5.9, witnessing that ChGO preserved its removal efficiency after the various cycles.

Moreover, ChGO sponges result biodegradable by microorganisms in soil.

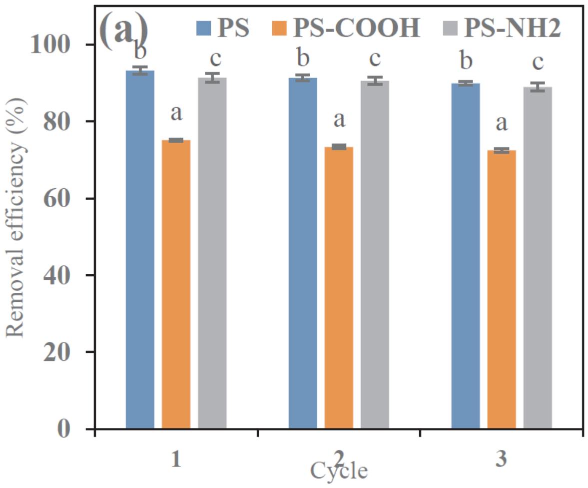

Figure 5.9 The removal efficiency of PS, PS-COOH, PS-NH2 by ChGO sponges in 3 cycles [19]

5.4 Summary and perspectives

Physical principles-based removal methods for removing MPs have been introduced in this Chapter. Specifically, these are: magnetic extraction, filtration and adsorption. Except for the filtration techniques, already partially applied in the water treatment plants, all the others are laboratory techniques still at an embryonic state of research. In fact, those presented are very recent studies, published in the last three years. The challenge is to adapt these techniques also on an industrial scale. Furthermore, it is important to improve the removal efficiency for the smallest MPs fractions.

6 Biological methods for MPs degradation

This category of methods is quite different from the previous ones. In fact, these techniques are based on a degradation process: MPs are transformed in other less polluting organic substances and are not physically removed.

6.1 Biofiltration for water treatment

In this case, the water to be treated is filtered through a porous organic material (also called *filter-bed*, represented in Figure 6.1) which serves as a support, and partly as nourishment, for aerobic microorganisms. The pollutants carried by the water flow are metabolized by the microorganisms which transform them into various reaction products, water and carbon dioxide (as waste substances).

Figure 6.1 *Typical filter-bed used in biofilters [55]*

This kind of filtration was only recently tested for MPs removal. For instance, a pilot-scale biofilter designed to remove pharmaceuticals, personal care products, and other organic micropollutants from WWTP effluents was chosen by Liu et al. [56] to evaluate the results in terms of MPs removal rates. Their evaluation included the removal efficiency in terms of MP mass and other considerations about sizes, masses, and polymer composition of the particles retained by the filter.

This filter was designed as shown in Figure 6.2. The biofilters were packed in circular stainless-steel tanks, and from top to bottom consisted of a sequence of layers of approximately 1.1 m of stone wool, 40 cm of Filtralite® CLEAN HR 3-6[7] and 10 cm

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[7] This material consists of high-density round clay aggregates with particle size ranging between 2,5 and 6 mm.

of granite sand (11–15 mm grain size). The different materials (stone wool, Filtralite, sand), and sampling valves on the side of the column were separated/covered by a layer of glass fiber to avoid migration of materials. This setup was fed with raw effluent for 2.5 months to ensure that biofilms had sufficiently matured. The filter was always kept submerged and the flow through the setup was driven by gravitation.

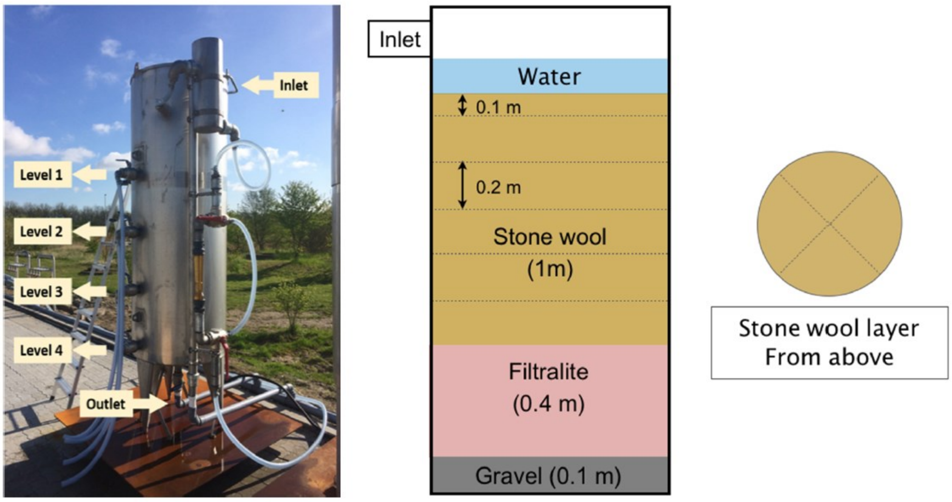

Figure 6.2 Overview of the biofilter. The effluent water from the treatment plant entered at the top (inlet) and was discharged at the bottom (outlet) [56]

There was a clear decrease in the MPs concentration from the inlet to the four sampled levels, as highlighted in Figure 6.3. Although there was a slight variation in concentration between the four levels inside the biofilter, no trend could be observed and the variation was most likely caused by random variations in the MPs content. Actually, the number of plastic particles identified in the samples was low and it may have introduced higher uncertainties.

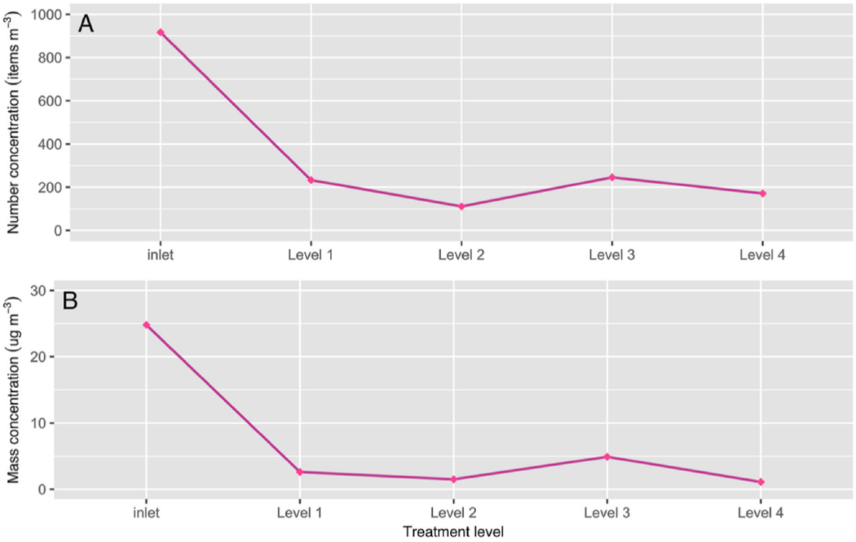

Figure 6.3 MPs number concentration (A) and mass concentration (B) of inlet and four sampling levels [56]

In conclusion, the investigated biofilter was able to reduce MPs in wastewater treatment plant by 79%–89%. The main part of this degradation occurred in the top of the biofilter, while the deeper layers only slightly retained MPs. In fact, no particles larger than 100 μm were found in the final effluent. Hence, the biofilter was able to lower the MPs concentration in the treated wastewater but did not ensure a complete retainment.

6.2 Microplastic degradation by microorganisms

Considering the marine environment, the degradation of polymers is generally driven by their interaction with ultraviolet (UV) light from the sun. UV radiation provides the activation energy required to initiate the oxidation of the polymers (*photo-oxidative degradation*) [26], which become brittle and start breaking in smaller parts [26] [22]. After several fragmentation steps, polymer chains reach a sufficiently low molecular weight and dimension. At this point, plastic materials can be metabolized by microorganisms, who can convert the carbon in the polymer chains to carbon dioxide or incorporate it into biomolecules. This process is called *biodegradation* [22]. Nevertheless, in a marine environment, the latter process is several orders of magnitude slower compared to light-induced oxidative degradation of plastics [26].

This degradative process promoted by microorganisms can be used to enhance MPs removal and this path has been followed in several studies. Auta et al. [57] isolated eight bacterial strains from a mangrove sediment in Peninsular Malaysia. These bacterial strains were studied for their potential to degrade UV-treated microplastics from polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), and polystyrene (PS). Only two of the eight bacterial colonies isolated, i.e. *Bacillus cereus* and *Bacillus gottheilii*, were able to grow on a synthetic medium containing MPs as the unique carbon source. Carbon is the microorganisms' nourishment; this is the reason why degradation process was monitored both by recording the weight loss of microplastics and the growth pattern of bacteria.

The biodegradation extent was validated by assessment of the morphological and structural changes through scanning electron microscopy and Fourier transform infrared spectroscopy analyses. The calculated weight losses percentage after forty days are reported in the following Table 6.1.

Table 6.1 *Calculated weight loss after forty days for bacillus cereus and bacillus gottheilii*

	Bacillus cereus	***Bacillus gottheilii***
PE	1.6 %	6.2%
PET	6.6%	3.0%
PP		3.6%
PS	7.4%	5.8%

The degradative process was confirmed by: the growth patterns of the isolates in microplastic-infused media, the formation of new functional groups, and the reduction in the absorption characteristic peaks of the microplastics from FTIR analysis, the weight loss, and the subsequent morphological changes observed in SEM images (Figure 6.4). SEM observation showed that after 40 days of incubation with the isolates, some of the microplastic surfaces became rough and possessed numerous holes/pores, erosions, cracks, and grooves. The uninoculated samples (control) remained smooth and unchanged. This result provided evidence for the deterioration of the microplastics.

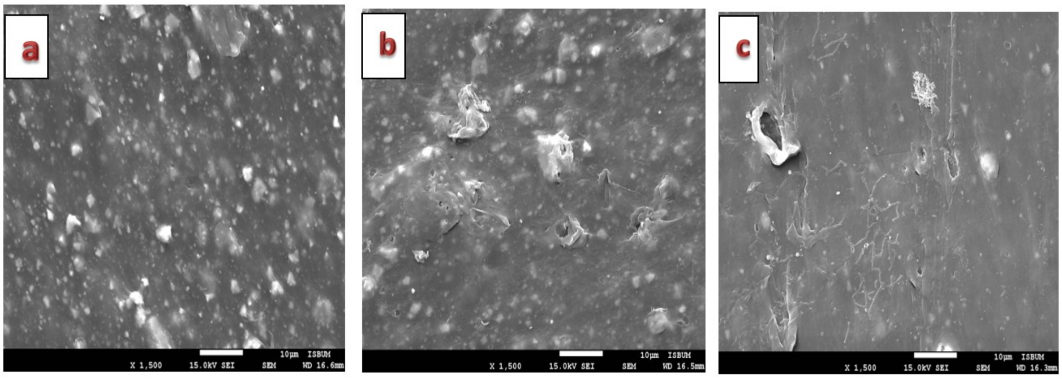

Figure 6.4 *SEM photograph of polyethylene (PE) after 40 days (a) Control (uninoculated with bacteria), (b) inoculated with Bacillus cereus, (c) inoculated with Bacillus gottheilii. The images show the formation of holes/pores on the PE surface with reference to the control [57]*

This strategy will potentially play a significant role related to the identification of suitable MPs degradation agents, avoiding the use of chemical treatments, avoiding the emission of potentially polluting substances into the environment.

7 Nanoplastics: planning of a research project for a sampling and analysis activity

7.1 Background

The literature analysis presented and summarized in this thesis work concerns MPs removal methods. One of the emerged limits is that none of these methods are effective in the removal of the smallest fraction of MPs, and therefore certainly will not be effective in the removal of plastic particles at the nanoscale (1-100 nm), commonly produced by the degradation of plastic materials. Very recently, nanoplastics (NPs) have become subject of interest for the scientific community due to the fact that NPs can be probably considered more harmful for human health.

As in the case of microplastics, studies about their toxicity are still at a preliminary stage and this is mainly due to the difficulties in finding suitable analytical methods for detecting MPs and especially NPs in complex matrices. Many of the published work have highlighted that the main source of MPs and NPs uptake is through oral ingestion. A number of different steps that involve the ingested particles lead to various kind of modification and interaction with the human organism. The particles may come in contact with digestive fluids, intestinal cells and organs as liver, and be transported around the organism, as well as be excreted (as shown in Figure 7.1). All these phenomena are strictly influenced by the dimension of the particles ingested and on their chemical composition. In particular, the crossing of the intestinal barrier occurs in a *size-dependent manner*, and only plastic particles smaller than 150 μm in size might in principle cross the intestinal epithelium. This is the reason why the ingestion of NPs seems to be more harmful compared to the ingestion of bigger plastic particles and this is alarming considering that most of the Food Contact Materials (FCM), for packaging or kitchenware, is constituted by plastic [58].

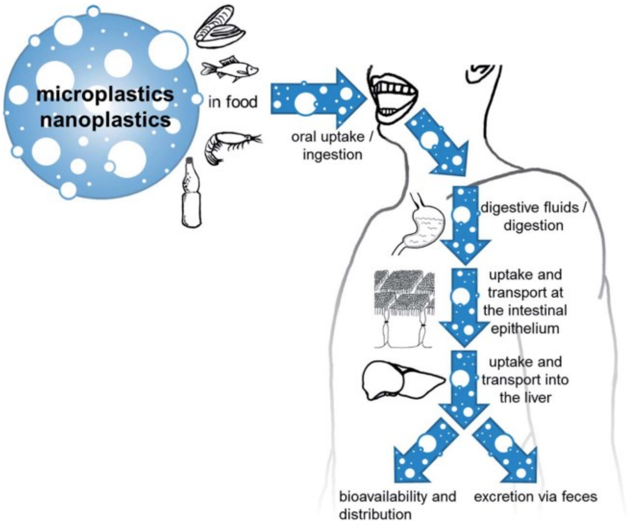

Figure 7.1 *MPs and NPs ingestion route [58]*

Furthermore, NPs are typically hydrophobic and this feature, combined with the dimensions, allow their entry into cells through poration or disruption of cell walls, which may lead to cytotoxicity. This cytotoxic effect has already been verified for a wide range of nanomaterials, including carbon nanotubes, quantum dots and silver nanoparticles, and concerns have been raised about the lack of regulations on the use of nanoparticles in cosmetics and foods in North America and Europe. Despite the potential severity of its environmental and health impacts, pollution with nanoplastics has been generally neglected, mainly because of methodological challenges [58].

Several studies have started approaching the topic ([59], [60]), but a systematic approach is still missing. For instance, Hernandez et al. [59] examined three commercial facial scrubs containing polyethylene (PE) microbeads (~0.2 mm diameter) to verify whether they contained also NPs. Firstly, facial scrubs were diluted (0.2 g of scrub in 10 mL of water). Then, particulates in the scrubs were fractionated through a sequential filtration, using Whatman filter paper[8] and negative pressure filtration, to isolate < 100 nm particles (as shown Figure 7.2). Scanning Electron Microscopy (SEM) was used to confirm the presence of nanoparticles ranging in size from 24 ± 6 to 52 ± 14 nm. X-ray photoelectron spectroscopy and Fourier Transform Infrared Spectroscopy were used to confirm that the identified nanoparticles consisted of PE. This study confirmed the unexpected presence of NPs in personal care products containing polyethylene microbeads and highlighted the need for further studies to characterize the distribution and the chemical nature of NPs found in aquatic and soil environments.

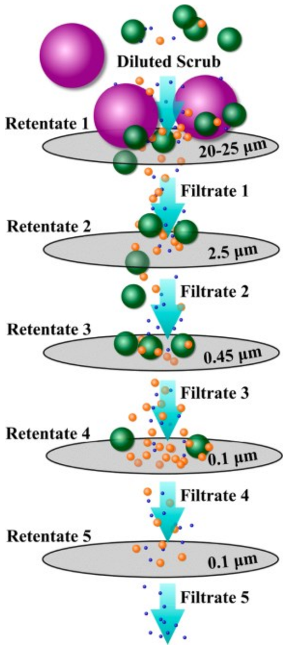

Figure 7.2 *Filtration Process [59]*

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[8] Commercial name of a typical filtering paper, available with different meshes

As a different example, Scott Lambert and Martin Wagner [60] applied nanoparticle tracking analysis to characterise the formation of NPs during the degradation of a polystyrene (PS) disposable coffee cup lid. In this case, the PS sample was cut into 1 cm squares (using scissors), placed in glass vials, immersed in 20 ml demineralized water, and placed in a weathering chamber used to simulate a typical degradation environment. The samples were exposed for 24 h to light in both the visible and ultra-violet (UV: 320 e 400 nm) range, in static conditions, at a fixed temperature of 30 °C. Samples were taken after 7, 14, 28 and 56 days of permanence inside the weathering chamber. Nanoparticle tracking analysis (NTA) was used to determine the particle size distribution in the liquid samples. NTA is a method for visualizing and analysing particles in liquids that relates the rate of Brownian motion to particle size. The rate of movement is related only to the viscosity and temperature of the liquid; it is not influenced by particle density or refractive index. In a Brownian motion, the diffusion constant D_t is related to the particle size through the *Stokes-Einstein equation* (Eq. 7.1) [61].

$$\frac{\overline{(x,y)^2}}{4} = D_t = \frac{TK_b}{3\pi\eta d} \tag{7.1}$$

Where:

$\overline{(x,y)^2}$ is the mean squared speed of a particle at a fixed temperature (T),
Dt is the diffusion constant, a product of diffusion coefficient *D* and time t,
Kb is Boltzmann's constant,
T is the absolute temperature,
η is the viscosity and
d is the hydrodynamic diameter of the spherical particle.

In NTA this motion is analyzed by video – individual particle positional changes are tracked in two dimensions from which the particle diffusion is determined. Knowing D_t, the particle hydrodynamic diameter can be then determined. Therefore, NTA allows for the determination of a size distribution profile of small particles with a diameter of approximately 10-1000 nm in a liquid suspension. In this study, NTA was used to demonstrate the formation of nanoplastics during the PS degradation process. The increase in the formation of nanoplastics is demonstrated by the particle size distributions obtained and shown in Figure 7.3. The blank samples are used to represent background concentrations, while the control samples are used to define any naturally occurring particles that may enter the samples during the exposure period (e.g. atmospheric dust).

Therefore, this research is useful to define one possible technique disposable to analyse NPs.

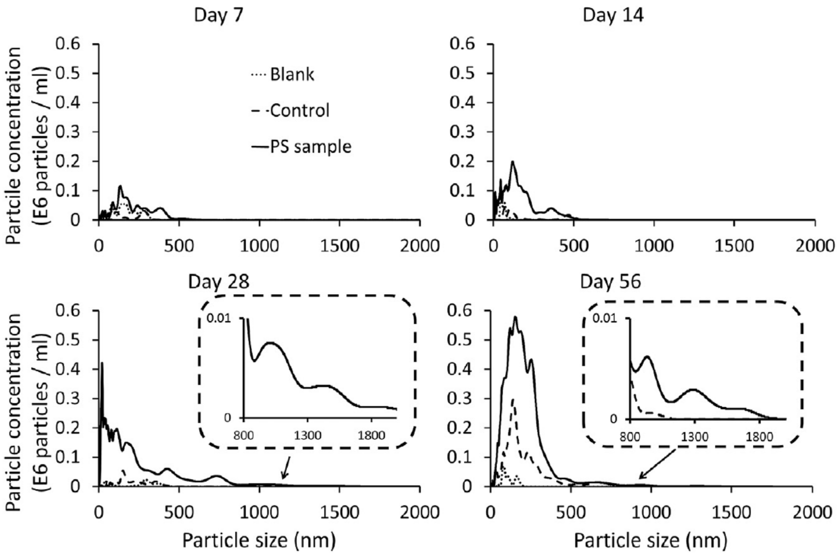


Figure 7.3 Size distribution data of particles formed during the degradation of a polystyrene coffee cup lid measured by nanoparticle tracking analysis [60].

The studies reported above are taken into account in the elaboration of this Chapter, whose aim is to provide a possible research path aimed at the development of a standard procedure for sampling and analysing NPs. Furthermore, a preliminary study of a filtering procedure using nanoporous graphene membranes is provided. These membranes are selected for this application considering the nearly frictionless surface that enables them to minimize transport resistance and maximize the permeate flux. In addition, the outstanding mechanical strength and chemical stability, together with cost-effective production, are other characteristics that allow to use graphene-based membranes for practical applications [62].

7.2 General information about the research activity

1 - Research Project Title

"Optimization of Nanoplastic sampling and analysis procedure"

2 - Duration (months)

5 months

3 - Key Words

- Nanoplastics
- Water pollution
- Materials characterization
- Membrane technology
- Nanoporous graphene

7.3 Purpose of the research activity

This project has two main objectives:

- Objective 1: Development of a standard procedure for sampling and analysing nanoplastics (NPs);
- Objective 2: Validation of the developed procedure to filtrate NPs using nanoporous graphene membranes.

7.4 Work packages and tasks involved

The project is organized in 4 work packages (WP) each one divided in tasks (T) and sub-tasks (ST).

1) **WP 1-Bibliographic Research and preliminary work**

The aim of this first WP is to obtain an overview of the current methodologies employed for the removal of MPs and NPs. The analysis of these methodologies paves the way for the determination of the best approach to be proposed in the subsequent work and represent benchmark approaches to compare with. At the same time, this step is important to properly schedule the experimental work.

Tasks:

- T1: Literature research activity: state of art of MPs removal methods
    - ST1: Critical analysis of articles, acts and specialized web sites.

- T2: Planning Activity

    - ST1: Gantt Chart

      This ST is necessary to properly set the work timeline and to establish a deadline for the entire project and for each ST involved.

    - ST2: SWOT Analysis

      Swot analysis is a strategic planning technique used to identify strengths, weaknesses, opportunities, and threats related to the project. It is intended to specify the objectives of the project with more details and identify the internal and external factors that are favourable and unfavourable to achieve those objectives.

    - ST3: Activities definition and preliminary study

      Definition of the activities necessary to achieve the objectives. Study and understanding of the best analysis techniques to achieve the intended objectives.

2) WP2-Sampling:

This WP aims at developing a standard working procedure to separate the smallest MPs and consequently, of NPs. This phase consists in a separation of the lightest fraction of particles from samples of discharge water. These samples could, for instance, be extracted from washing machines discharge water after a few washing cycles, possibly with a high number of spin cycles.

The techniques proposed are inspired by the studies presented in paragraph 7.1. and by the results emerged by the literature previously presented in this thesis.

Milestone: Selection of the best procedure. This implies a certain number of tests to optimize all the process parameters involved.

Tasks:

- T1: Coarse Filtration
  Inspired from [58], a four-step filtration, using a filtering paper, is provided.
    - ST1: Filtering Paper (20-25 μm)
    - ST2: Filtering Paper (2.5 μm)
    - ST3: Filtering Paper (0.45 μm)
    - ST4: Filtering Paper (0.1 μm=100 nm)

- T2: Centrifugal separation
  Centrifugation is a separation technique used for heterogeneous systems when the density difference between the two substances involved is quite small. Therefore, this technology is suitable for NPs-Water systems in which particles are light, small and with a density proximal to the water's one. Due to the centrifugal acceleration imposed, the heaviest particles tend to sediment, while the lightest remain onto the surface and then are collected.

- T3: Reverse Osmosis
  Reverse Osmosis (RO) is used in industrial water treatment systems. These processes typically use nonporous or nanofiltration membranes (pore size < 2 nm) for the removal of salts, contaminants, heavy metals, and other impurities. The application of a high pressure (10-100 bar) to a concentrated water solution forces the water through a semipermeable membrane, leaving all the contaminants (NPs) in a more concentrated water solution.

3) WP3-Analysis:

The purpose of this WP is to characterize the particles, both from dimensional and chemical point of view. The proposed techniques for the dimensional characterization of NPs are chosen taking inspiration from the more common techniques used in literature in the field of nanomaterials, while the proposed chemical analysis techniques are inspired to the ones used for MPs and previously presented in this thesis work.

Milestone: Selection of the best characterization approach or combination on them. This implies a certain number of tests to optimize all the process parameters.

Tasks:

- T1-Dimensional characterization of the nanoparticles
    - ST1-Dynamic Light Scattering

      Dynamic Light Scattering (also known as Photon Correlation Spectroscopy) is used to determine the size of particles. Shining a monochromatic light beam, such as a laser, onto a solution with spherical particles in Brownian motion causes a Doppler Shift when the light hits the moving particle, changing the wavelength of the incoming light. This change is related to the size of the particles. It is possible to compute the sphere size distribution and give a description of the particle's motion in the medium, measuring the diffusion coefficient of the particle and using the autocorrelation function [63].
    - ST1 (alternative)- Nanoparticle Tracking Analysis (NTA)

      It can be used as an alternative technique to DLS as suggested by Lambert *et al.* A comparison between DLS and NTA is shown in Table 7.1.
    - ST2-Electron microscopy

      Electron Microscopy is used to analyse the morphology of particles. The aim of this kind of study is understanding the possible shape of NPs produced.

Table 7.1 *Comparison between DLS and NTA [61]*

	DLS	NTA
Characteristics		
Size accuracy	Accurate for monodisperse samples, inaccurate for polydisperse samples	Accurate for both monodisperse and polydisperse samples
Peak resolution	Low (>3 fold difference in diameter)	High (<0.5 fold difference in diameter)
Size range	Ca. 1–1,000 nm	Ca. 30–1,000 nm
Concentration range (particles/ml)	Broad (about 10^8–10^{12})	Limited (10^7–10^9)
Population ratio	Narrow range Large influence on size accuracy and distribution	Very broad range Very little influence on size accuracy and little influence on size distribution
Reproducibility	More reproducible	Less reproducible
Contaminations	Large particles can seriously compromise the results	Dust, microorganisms or aggregates easily detected, large particles have little influence
Operational		
Device handling	Very user-friendly Little sample handling Possibility of using disposable cuvettes	Requires several parameter adjustments Sample handling may affect size distribution Sample chamber must be cleaned after each sample Experienced operator required
Time consumption	Between 2 to 5 min per measurement	Between 5 min to 1 hour per measurement
Particular output	Approximate size distribution Intensity distribution Z-ave PdI	Individual particle sizing Number distribution Approximate concentrations Individual particle intensity
Sample visualization	No	Yes
Applications		
Drug delivery nanoparticles	Accurate sizing Approximate size distribution Hard detection of contaminants	Accurate sizing More reliable size distribution Easy detection of contaminants
Protein aggregates	Approximate size distribution Includes protein monomers and some excipients Presence of very large aggregates has a big impact on the result	Accurate size distribution Protein monomer and small aggregates excluded Aggregate architecture information Interference of large aggregates may sometimes be overcome

- T2- Chemical characterization of the nanoparticles

  The aim of this task is to define the chemical nature of NPs. This information is useful also to speculate possible origins for the plastic particles. Among others, this is done using two main spectroscopy techniques, as suggested by the literature concerning MPs and presented into the previous chapters, and by Hernandez et al. [59].

  - ST1: IR spectroscopy
  - ST2: Raman spectroscopy
  - ST3: ζ-Potential analysis (coupled with DLS)

    The zeta potential is an indicator of the stability of colloidal dispersions. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in a dispersion. In particular, when the potential is small, attractive forces may exceed this repulsion and the dispersion may break and flocculate.

4) **WP4-Filtration tests:**

The last part of the work is dedicated to a preliminary study of possible removal methods for NPs once the largest MPs fraction has been removed. The method chosen to achieve this goal is a filtration process using nanoporous graphene membranes.

Tasks:

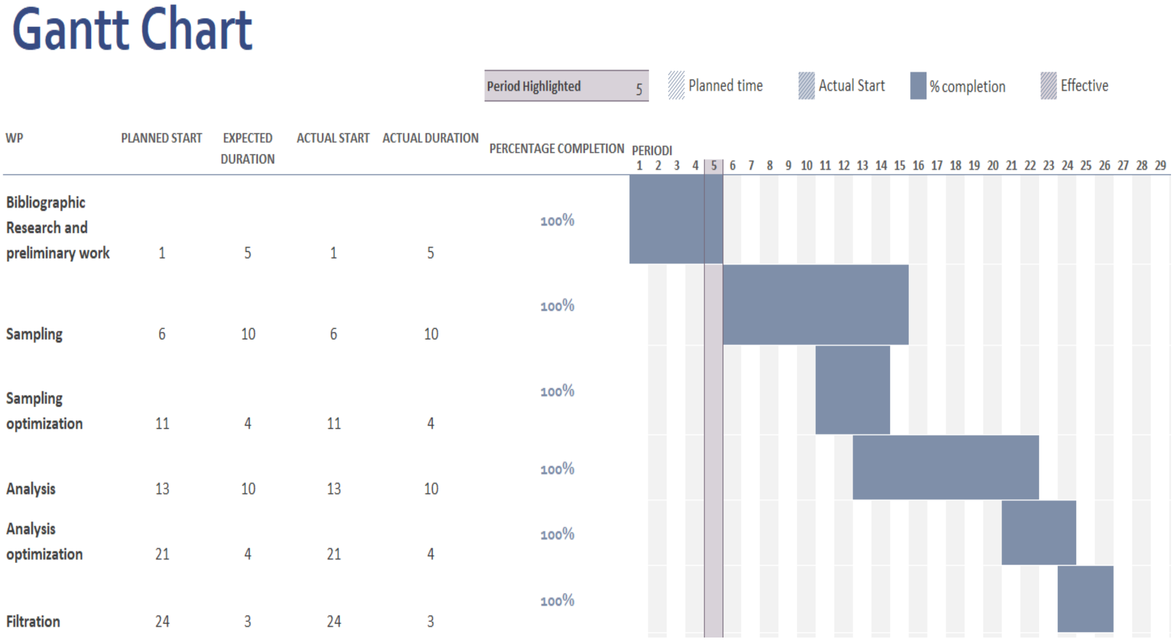
- T1- Fabrication of nanoporous graphene membranes.
- T2- Real study of the filtration properties of nanoplastics using the membranes developed in the previous task T1.

7.5 Planning and project management

Project's scheduling is done using a Gantt Chart (Figure 7.4), i.e. a bar diagram used to simply show the development in time of all the project's tasks.

In this case, a period is assumed equal to one week of work. Considering all the planned activities, the expected time to achieve the goals introduced in Paragraph 7.2, is of 26 weeks (about 5 months).

This kind of scheduling is referred to an ideal condition of work. The current pandemic situation could slow down the various WP. Overall, this thesis work covers the activities of WP1- " Bibliographic research and preliminary work".



WP	PLANNED START	EXPECTED DURATION	ACTUAL START	ACTUAL DURATION	PERCENTAGE COMPLETION
Bibliographic Research and preliminary work	1	5	1	5	100%
Sampling	6	10	6	10	100%
Sampling optimization	11	4	11	4	100%
Analysis	13	10	13	10	100%
Analysis optimization	21	4	21	4	100%
Filtration	24	3	24	3	100%

Figure 7.4 *Gant Chart for the research project*

7.6 SWOT analysis

The SWOT analysis consists in analysing four parameters characterizing a research plan, namely:

- Strengths: characteristics of the research project that give it an advantage over others.
- Weaknesses: characteristics that place the research project at a disadvantage relative to others.
- Opportunities: elements in the environment that are advantageous for the project.
- Threats: elements in the environment that are disadvantageous for the project.

While strengths and weaknesses are frequently internal, opportunities and threats are more commonly external.

In this context, a short SWOT analysis (reported in Table 7.2) is useful to make self-criticism and to find possible drawbacks and critical points for success of the project.

***Table 7.2** SWOT analysis of the project*

Strengths	Weakness
▪ Trending and sound topic ▪ Few Researches about ▪ Lack of a standard and common procedure for NPs sampling and analysis ▪ The proposed method is inspired to well-known techniques used in the field on nanomaterials	▪ Several complex tests involved ▪ Time required for each test and consequent validation ▪ Optimization is required ▪ Not easily scalable on industrial scale
Opportunities	**Threats**
▪ The project meets the requirements the ONU 17 sustainable development goals (3, 6, 11, 12, 14) (Figure 7.5)	▪ CoVid-19 Pandemic

Figure 7.5 ONU 17 development goals

7.7 Conclusions: critical points

This chapter introduced a possible research plan with two main objectives: the development of a standard procedure for sampling and analysing nanoplastics and the validation of the developed procedure to filtrate NPs using nanoporous graphene membranes.

The proposed procedure is inspired to classical analysis used to characterize colloidal suspensions and it takes into account the literature analysed in the previous chapters of this work, mostly for what concerns the characterization techniques.

Several drawbacks are inherent in the method itself: firstly, the several tests involved are complex and time consuming. Furthermore, each test requires validation and optimization in order to obtain the best testing parameters.

These are the critical points that have to be deepened in future and with a real testing phase.

8 Conclusions

The purpose of this work is to provide a systematic description of the techniques currently available to limit or to avoid the emission of microplastics into the sea through wastewater, as well as to provide a research plan to develop a standard procedure for nanoplastics (NPs) sampling, analysis and removal. To this aim, a bibliographic research consulting scientific articles, conference proceedings and specialized internet sites was first carried out. The final objective is to present an overall and complete view of MPs issue, discussing both consolidated large-scale solutions and processes that are currently being tested at the lab scale only for MP removal. The last part of this work which focuses on the analysis and removal of NPs, aims at covering a current literature lack going beyond the state of art.

The analysis of the chemical composition of the MPs released in the environment revealed that the most common polymers found in microplastics are PET, PP, PE and PA. Furthermore, the particles are often characterized by a fibrous morphology. For these pollutants, the main results in terms of efficiency for the mitigation actions and for the removal methods are reported in Table 8.1 and Table 8.2, respectively.

Table 8.1 *MPs emission reduction rate for mitigation actions*

Mitigation Action	MPs emission reduction rate
Pectin- Surface Treatment	90%
PLA- Surface Treatment	80%
PBS- Surface Treatment	80%

Table 8.2 *MPs removal rate*

Removal Method	MPs removal rate
Membrane Bio Reactor[9]	99.9 %
Rapid Sand Filter[1]	97%
Dissolved Air Flotation[1]	95%
Discfilter[1]	40-98.5%
Aggregation processes	Function of the volume obtained
Magnetic Extraction	92-93%
Reverse Osmosis[1]	66.7%

In addition to the methods reported above, techniques related to the biodegradation of plastic materials have been also presented. In particular, it was

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[9] Tertiary stage of treatment

observed a decrease of almost 79-89% in mass in the case of biofiltration, while considering the action of microorganisms the results are summarized in Table 8.3.

Table 8.3 *MPs removal by microorganisms: calculated weight loss after 40 days for bacillus cereus and bacillus gottheilii*

	Bacillus cereus	***Bacillus gottheilii***
PE	1.6 %	6.2%
PET	6.6%	3.0%
PP		3.6%
PS	7.4%	5.8%

The analysed techniques certainly proved to be promising in terms of emission prevention and removal of MPs. In particular, it should be highlighted that on average the removal rates are higher than 80% and the highest efficiencies (> 90%) are achieved only when several techniques are coupled together. Indeed, at least one tertiary stage of treatment must be provided in water treatment plants. Efficiencies would improve if also a mitigative action is provided (no studies have been carried out in this direction yet). In general, all methods presented in the literature are not effective in the removal of the smallest MPs fraction (1-10 μm or up to 100 μm if a tertiary stage of treatment is not provided) and therefore certainly prove to be ineffective in the removal of NPs. NPs are even more dangerous than other MPs, as they can penetrate the intestinal epithelium. It is important to highlight how studies involving nanoplastics have long been slowed down by the lack of a standard procedure for sampling and analysis. For this reason, this thesis work provides a research plan describing a possible path for the development of a standard procedure for NPs sampling and analysis. In setting up the research plan we got inspired by the MPs literature presented in the first part of the thesis and by common analysis practices usually applied to colloidal systems.

The expected results for this project are the development of a standard procedure for sampling and analysing nanoplastics, and the validation of the developed procedure to filtrate NPs using nanoporous graphene membranes. Several drawbacks are inherent in the proposed method itself: firstly, the large number of tests involved which are complex and time consuming. Moreover, each proposed test requires validation and optimization in order to identify the best testing conditions. These are the critical points that must be deepened in the future with lab testing phase.

9 List of symbols and abbreviations

- MPs: Microplastics
- NPs: Nanoplastics
- WWTPs: Wastewater Treatment Plants
- WTPs: Water Treatment Plants (drinking water)
- DAF: Dissolved Air Flotation
- RSF: Rapid Sand Filter
- DC: Disc Filter
- GAC: Granular Activated Carbon
- CASP: Conventional Activated Slug Process
- MBR: Membrane Bioreactor
- UF: Ultra Filtration
- NTA: Nanoparticle Tracking Analysis
- DLS: Dynamic Light Scattering

10 List of Figures

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